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DEVELOPMENT OF ORGANIC SEALANTS FOR APPLICATIONS AT VERY LOW TEMPERATURES

Summary Report — Second Year

30 June 1963

AEROSPACE ENGINEERING DIVISION

HUGHES

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CULVER CITY, CALIFORNIA

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HUGHES AIRCRAFT ~~COMPANY~~

AEROSPACE GROUP

MATERIALS TECHNOLOGY DEPARTMENT

Culver City, Cal~~ifornia~~ Aerospace Engineering Div.

DEVELOPMENT OF ORGANIC SEALANTS FOR APPLICATIONS AT VERY LOW TEMPERATURES

by

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30 June 1963 95p mf

Summary Report Covering
the Period 1 July 1962 to 30 June 1963

(NASA Contract No. NAS 8-2428
Control No. TP-85150 and TP-85150 S1

George C. Marshall Space Flight Center,
NASA, Huntsville, Alabama

Approved: W. H. Colner
Manager, Materials Technology Department

FOREWORD

This report was prepared by the Hughes Aircraft Company to cover the work completed during the period 1 July 1962 to 30 June 1963 under a contract for the development of sealant materials for use in the extremely cold environments of launch vehicles. The contract is sponsored by the George C. Marshall Space Flight Center, NASA, Huntsville, Alabama, with Clyde M. Holmes as Project Engineer.

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The most promising candidate LOX-safe sealant was found to be Kel-F 800 resin reinforced with glass fabric and using a Kel-F 800 based hot melt primer. It has enough flexibility at 76°K to pass the bend test and its peel strength at 76°K is felt to be adequate. It failed to pass the contractor's impact test, however, and does not qualify as being LOX-safe. This was attributed to residual solvents left in the polymer after application. Adiprene L-100 cured with castor oil and RTV-X511 silicone remain as the best cryogenic sealants, when reinforced with glass fabric, for use in a non-LOX environment. Shock and vibration tests, at 76°K, were performed on these materials. The synthesis of a LOX-safe fluorinated polymer was attempted by preparation of a polyester from hexafluoroglutaric acid and hexafluoropentanediol, but no method was found to cure it because of its complete lack of solubility. Work on silicone polymers was continued. These were prepared by equilibration of tetravinyltetramethylcyclotetrasiloxane, tetrabutyltetramethylcyclotetrasiloxane, and octamethylcyclotetrasiloxane, using tetrabutylphosphonium hydroxide as catalyst. They were cured with dicumyl peroxide, but did not pass the low-temperature flexibility test even when reinforced with glass cloth. However, the thermal contraction of these polymers is similar to that of some of the commercial silicones which have passed the low-temperature flexibility test. A foamed sealant, based on the Adiprene system, was developed for sealing the weld line crevice of the dome LOX tanks. It is intended for the surfaces outside the LOX chamber. Material and process specifications were written and are given in the Appendix.

AUTHOR

I. INTRODUCTION

This report summarizes the work and accomplishments of the second year of this investigation.

The basic goals of the second year's program remained the same as those of the first year: to find or develop curable sealants, capable of field use, that can be applied by brush, spatula or caulking gun, and that will resist stresses at temperatures down to 20°K. The approach was to screen existing polymer systems having the lowest possible glass transition temperature and the least tendency for crystallization, to modify these polymers to achieve better low temperature properties through compounding modifications, and to synthesize new polymers whose molecular structures give promise of having better low temperature flexibility.

The screening of candidate materials for use as cryogenic sealants consisted of measuring their flexibilities at 76°K and observing their thermal contraction characteristics and volume changes down to 76°K. It is required that the sealants exhibit a degree of ductility or lack of brittleness at these temperatures, that their coefficients of thermal contraction closely match those of the metal substrates, and that volume changes at transition temperatures be minimal.

For the most part, the second year's program was a continuation of the first year's work. It was directed toward an exhaustive evaluation of basic polymer systems and existing compounded systems and the modification of both to upgrade their low-temperature properties through further compounding and reinforcing. In addition, considerable efforts were made to synthesize new polymers with improved low temperature properties and to solve specific hardware problems as directed by the Contractor.

During the year, the Contractor's representative requested that the prime effort be devoted to development of sealants compatible with liquid oxygen (LOX). Therefore, most of the effort was directed to this end and secondary effort was directed to the original target requirement of flexibility regardless of LOX sensitivity, at temperatures down to 20°K.

II. EVALUATION OF MODIFIED SEALANT MATERIALS

To evaluate sealant materials, candidate sealants were subjected to a low temperature flexibility test in an apparatus similar to that described in MIL-S-8516 but modified by the addition of insulating walls. This apparatus is used to bend test specimens over a 4-inch diameter mandrel. The test specimens consist of a strip of 0.032 x 1 x 6 inch aluminum coated to a nominal 1/16 inch with a sealant to be evaluated. The apparatus was cooled first with dry ice and then with liquid nitrogen. The test specimen was cooled with liquid nitrogen in a Dewar and subsequently inserted in the apparatus. Liquid nitrogen was allowed to flow over the specimen for one minute and the specimen was then subjected to a 4-inch radial bend. A schematic drawing of this apparatus is shown in Figure II-1. This liquid nitrogen bend test was used for screening purposes and materials that exhibit some flexibility by this test will later be subjected to the same test at liquid hydrogen temperature.

The aluminum strips themselves were prepared by cleaning through immersion in a hot solution of sodium dichromate in dilute sulfuric acid. Since it is rather impractical to use such a method for cleaning metals in the field, a modified formulas has been developed. Essentially, Cab-O-Sil is added to the solution to make a paste:

Water	30 g.
Concentrated Sulfuric Acid	10 g.
Sodium dichromate	1 g.
Cab-O-Sil	14 g.

The paste was applied to the aluminum surface at room temperature. After approximately 30 minutes, the paste was rinsed off with tap water. The aluminum surface was rinsed with distilled water and allowed to dry in air.

CANDIDATE LOX-SAFE SEALANTS

Existing LOX safe polymer materials available for investigation are quite limited in number. Fluorocarbon elastomers appear to be

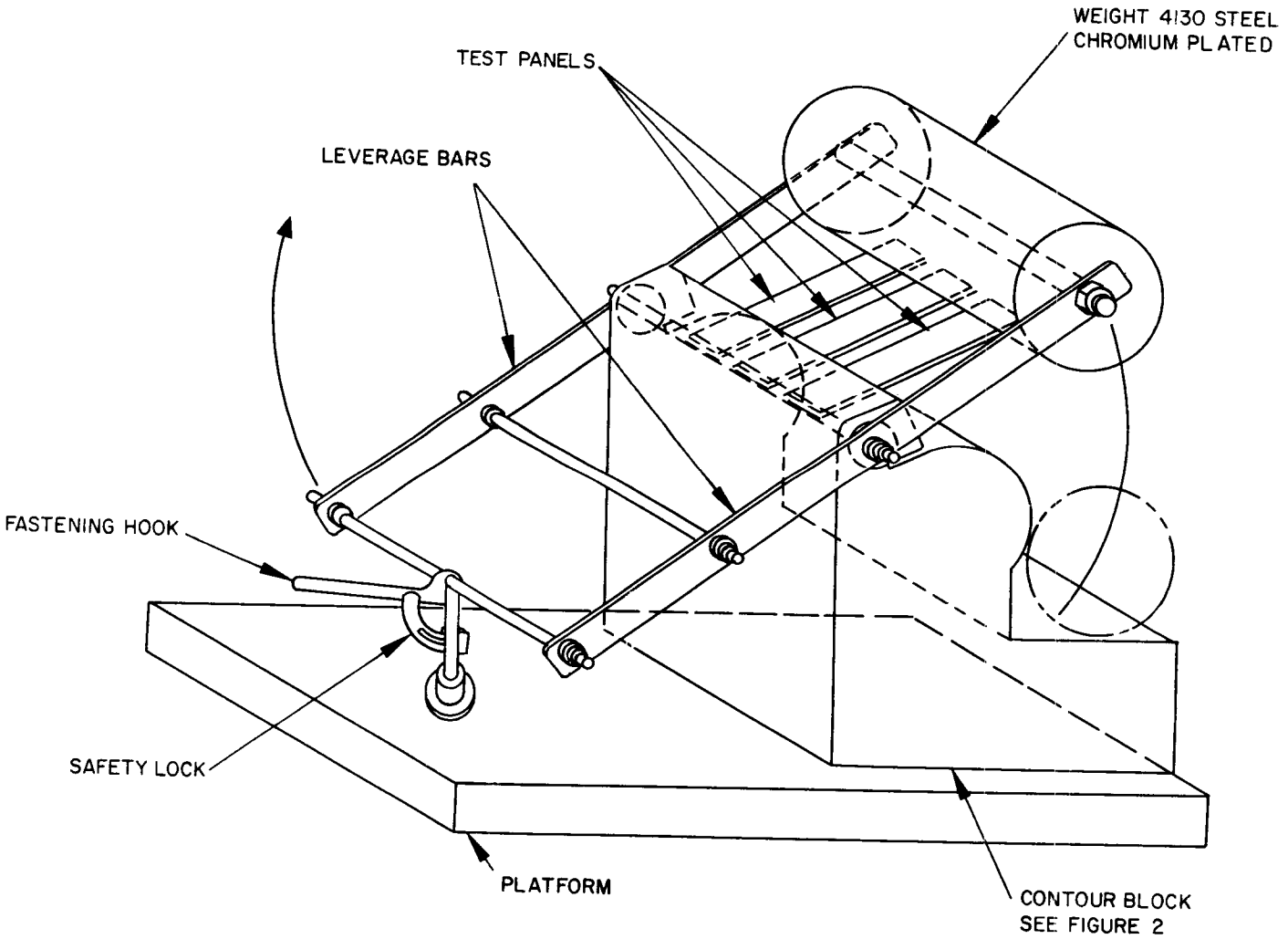


Figure II-1. Low temperature flexibility test.

the most promising, but they must be capable of being cured in place and have consistencies that would allow physical property improvements through modifications or reinforcements. A literature search indicated only two possible materials to be available which meet these requirements.

The first material selected was Kel-F Resin 800, manufactured by Minnesota Mining and Manufacturing Company. It is supplied as a solid and can be dissolved in a variety of solvents. In use, therefore, it would not be cured or cross-linked but would be deposited as a slightly flexible and tough solid after the solvent has evaporated. Care would have to be taken to protect the sealed surfaces or joints from solvents that could again attack the resin.

Preliminary bend test specimens were made by dissolving the resin in toluene and applying the solution to cleaned and etched 0.032 x 1 x 6 inch aluminum strips. The solvent was carefully removed in an oven maintained at 125°F to keep frothing at a minimum. To one set of specimens, fused silica was added as a reinforcing filter. The formulas tested are given in Table II-I and pictures of the specimens, after testing, are shown in Figure II-2.

Both the filled and unfilled specimens (FN 1 and FN 2) failed the bend test, at 76°K. The mode of failure, however, suggested that glass fibers or glass fabric could improve the physical properties.

Methyl isobutyl ketone, by itself or in combination with toluene, was subsequently found to be a slightly more efficient solvent than toluene alone. Moreover, it was more easily removed from the resin after application, leaving a resin layer that was much less porous. This solvent system was used for subsequent sealant formulations, as listed in Table II-II, Formulation Numbers FN 1 through 4.

Based on results of the preliminary screening, further tests were made on specimens compounded with various reinforcing fillers, curing agents, and primers. The modifications are detailed in Table II-II as FN-1 through FN-5. Photographs of the specimens after application of the low temperature flexibility test are shown in Figure II-3.

The first three of these specimens were prepared by filling solvent-borne Kel-F800 with Fiberfrax (refractory short strand fibers

FN*	Composition	Amount	FN*	Composition	Amount
1	Kel-F800 Resin	25.0 g	2	Kel-F800 Resin	25.0 g
	Toluene	100.0 cc		Toluene	100.0 cc
				Fused Silica, 200 Mesh	20.0 g

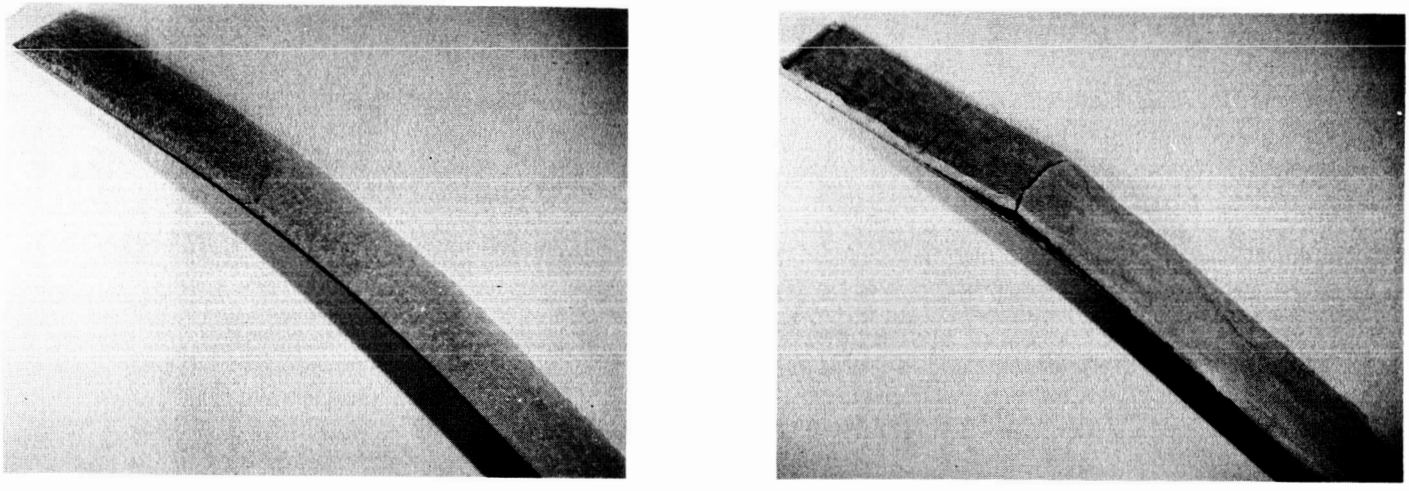
Table II-I. Sealants screened.

manufactured by the Carborundum Company) using either open weave glass "boat cloth", or 181 style glass fabric. Specimens made according to formulation FN-1 failed the flexibility test at 76°K, but there was fairly good adhesion to the aluminum substrate. Specimens of FN-2 and FN-3 were reinforced sufficiently so they did not break in the test, but also they did not adhere well to the aluminum and separated from the substrate. The primer was changed in FN-4 to try to improve adhesion of the Kel-F800 reinforced with glass cloth, but, as in the case of FN-3, the specimen pulled away from the aluminum substrate in the flexibility test.

The adhesion of solvent solutions of fluorocarbons to metallic surfaces appears to be a problem. A solution was investigated in terms of a new primer. In FN-5 (Table II-II), Minnesota Mining and Manufacturing Company HC912 primer for Kel-F800 was used. This material is solvent bourne and did not work well when the solvent solution of Kel-F800 was applied to the dry primer surface. The primer was attacked, exposing unprimed substrate surface to the Kel-F800. However, direct addition of the HC912 primer to the Kel-F800 solution before application to the aluminum substrate was found to improve adhesion. The solvent solution of Kel-F800 plus primer was applied to the 181 glass fabric strips and the solvent was allowed to evaporate until the prepreg strips were only slightly tacky. After the six plies were pressed together and applied to the aluminum substrate, the system was cured by solvent removal at 40°C overnight. When the specimen was subjected to the low-temperature flexibility test, there

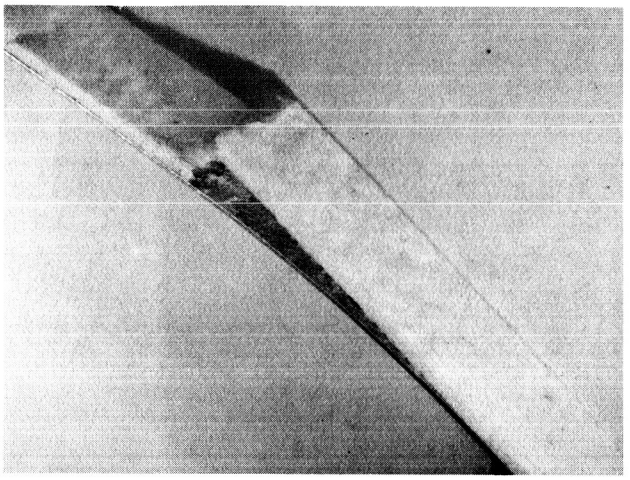
FN*	Composition	Amount	FN*	Composition	Amount
1	Kel-F800	10.0 g	5	Kel-F800	100.0 g
	Methyl Isobutyl Ketone	25.0 ml		Ethyl Acetate	100.0 ml
	Toluene	15.0 ml		3 M HC912 Primer	10.4 g
	Fiberfrax	12.5 g		181 Glass Cloth - 6 Plies	
	Chemlok 607 Primer				
2	Kel-F800	10.0 g	6	Viton A	25.0 g
	Methyl Isobutyl Ketone	25.0 ml		Ethyl Acetate	
	Toluene	15.0 ml		Triethylene Tetramine	7 drops
	Boat Cloth - 4 Plies			181 Glass Cloth - 4 Plies	
	Chemlok 607 Primer				
3	Kel-F800	20.0 g	7	Viton A	100.0 g
	Methyl Isobutyl Ketone	50.0 ml		Methyl Ethyl Ketone	200.0 ml
	181 Glass Cloth - 6 Plies			Triethylene Tetramine	1.0 g
	Chemlok 607 Primer			181 Glass Cloth - 6 Plies	
4	Kel-F800	40.0 g	8	Viton A	25.0 g
	Methyl Isobutyl Ketone	100.0 ml		LD 227	75.0 g
	181 Glass Cloth - 6 Plies			Methyl Ethyl Ketone	150.0 ml
	Viton A (100 g) + Methyl Ethyl Ketone (200 ml) + Triethylene Tetramine (3 g) as Primer			Triethylene Tetramine	2.5 g
				181 Glass Cloth - 4 Plies	
*FN = Formulation Number					

Table II-II. Sealant modification formulations.

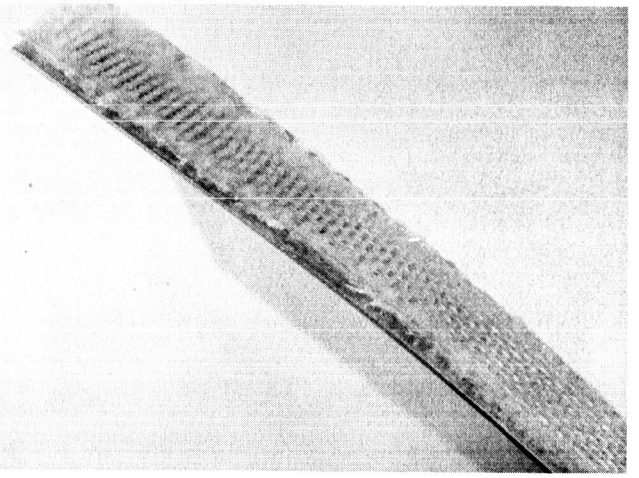


FN-1 FN-2

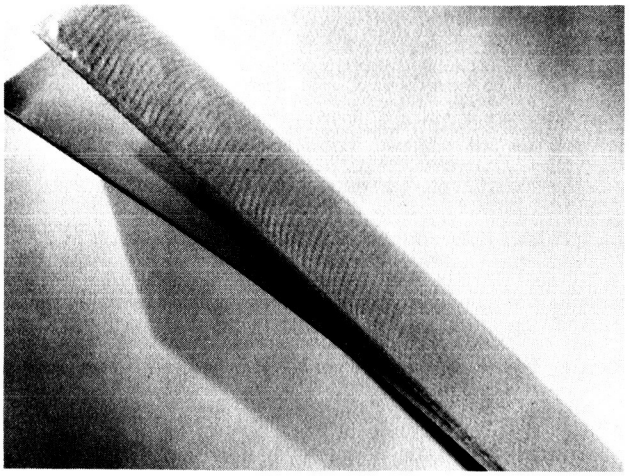
Figure II-2. Photographs of bend test specimens.



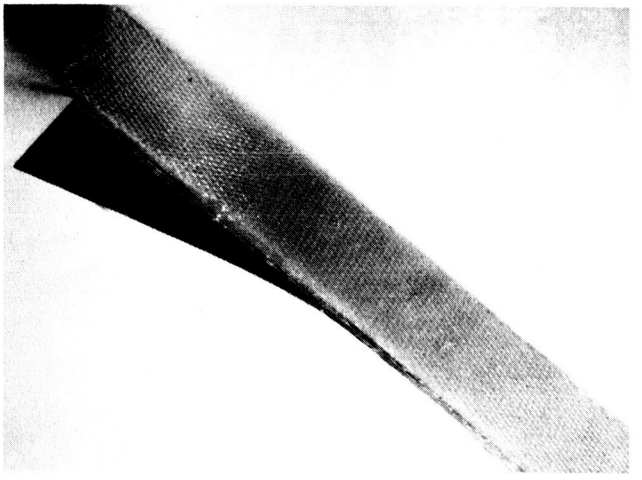
FN-1



FN-2

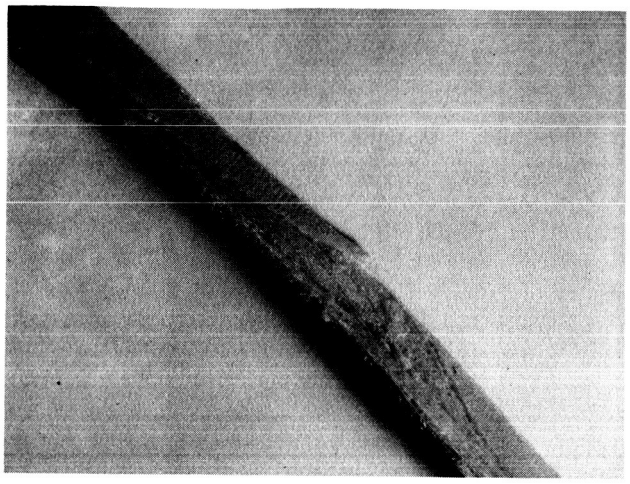


FN-3

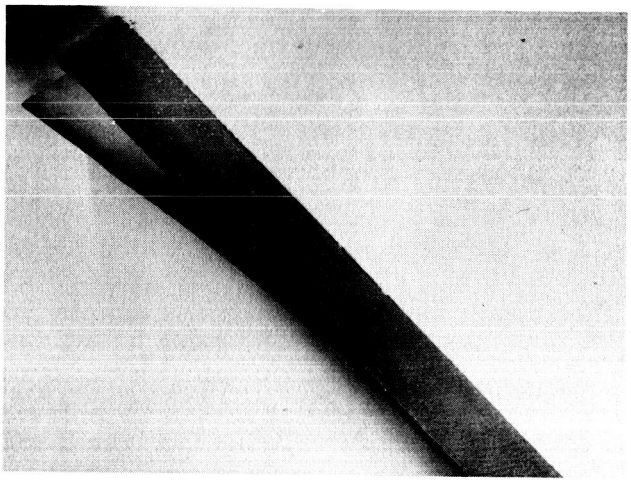


FN-4

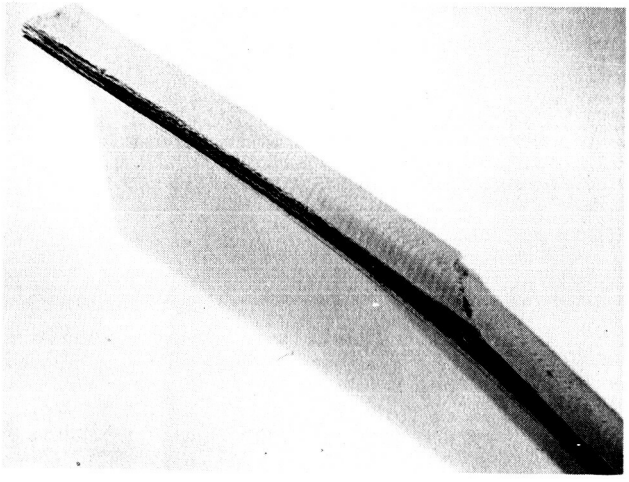
Figure II-3. Low temperature flexibility test - modifications.



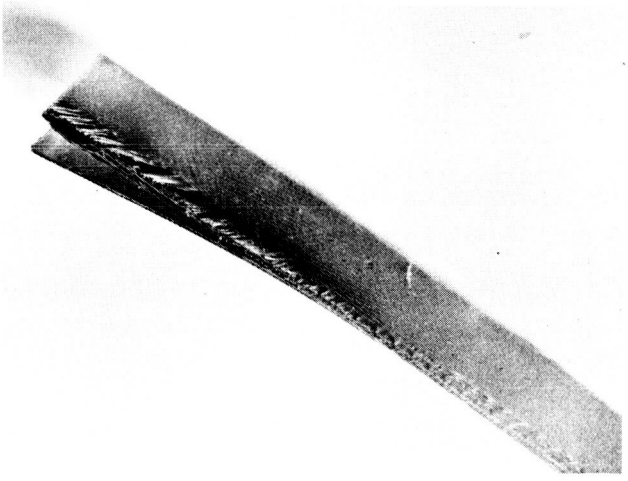
FN-5



FN-6



FN-7



FN-8

Figure II-3. Low temperature flexibility test - modifications (continued).

was sufficient adhesion to the aluminum substrate so that there was a failure of the top ply before the plies pulled away from the metal.

Efforts to improve the Kel-F system were continued. A solvent-free system of Kel-F800 and HC912 primer was prepared, which was suitable for application as a primer to the aluminum substrate by a hot-melt technique. Evaluation of this primer is discussed a few paragraphs further on.

Although the Vitons are not generally considered to have much flexibility at very low temperature, their usefulness in LOX warranted efforts to improve their physical properties. Viton A (FN-6 and FN-7, Table II-II) and mixtures of Viton A with LD 227 (FN-8), a low viscosity fluoroelastomer of the Viton family, were prepared with glass cloth reinforcement, but again there was a problem of adhesion to the aluminum substrate. Where the specimen did adhere, it exhibited brittle failure.

Failure to develop a suitable modified LOX-Safe sealant caused the emphasis by the investigators to be shifted toward synthesizing new polymers. (The synthesis phase of the program is discussed later in this report.) However, efforts to modify and improve existing sealants were continued, as described below.

The materials discussed above failed due either to lack of adhesion to the aluminum substrate or to fracture of the elastomers during flexibility tests. Therefore, a composite of a good primer and reinforced elastomer with good flexibility at low temperatures is required. During the quarter ending 15 March 1963, additional LOX-Safe sealant modifications were developed. To satisfy the first requirement, that of a primer, a hot melt primer was developed. The primer consists of Kel-F 800 resin, manufactured by the Minnesota Mining and Manufacturing Company, HC-912 primer concentrate, also from 3M, and methyl ethyl ketone. To facilitate its use, the primer was made in the following way: 100 gm. Kel-F 800 was dissolved in 200 gm. methyl ethyl ketone. To this solution, 25 gm. of HC-912 concentrate (5.25 gm. solids) was added. The solution was then washed with hexane to remove the methyl ethyl ketone, and the solid materials were dried at 30°C

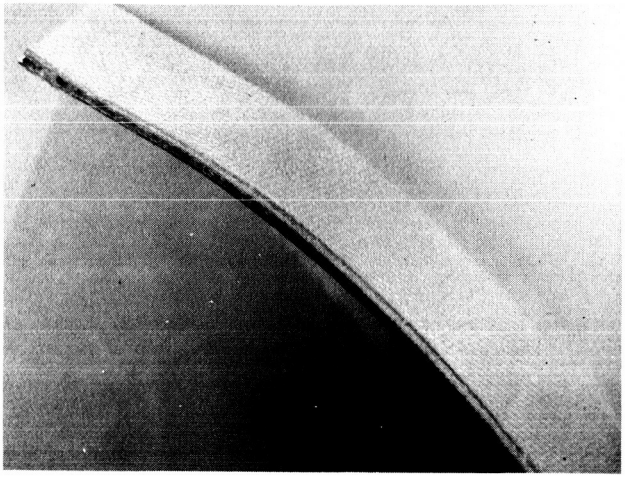
until almost all of the hexane was removed. The primer was then applied in a thin film to aluminum strips heated to approximately 145°C in an oven or by a heat gun. In this process, the primer "stick" was rubbed over the hot metal surface. The observed adhesion, using Kel-F formulations on etched aluminum, was satisfactory and this primer was used on all subsequent test specimens. This material was sent to NASA for LOX impact testing, the results of which are described in a subsequent part of this section.

To satisfy the second requirement, that of a reinforced elastomer with good flexibility at low temperatures, screening was continued on sealant formulations based on modifications of the Kel-F 800 resin. This material was supplied as a solid that can be dissolved in a variety of solvents and applied to surfaces to be sealed. When the solvent was driven off through heating, a slightly flexible and tough solid remained that was reputed to be LOX safe.

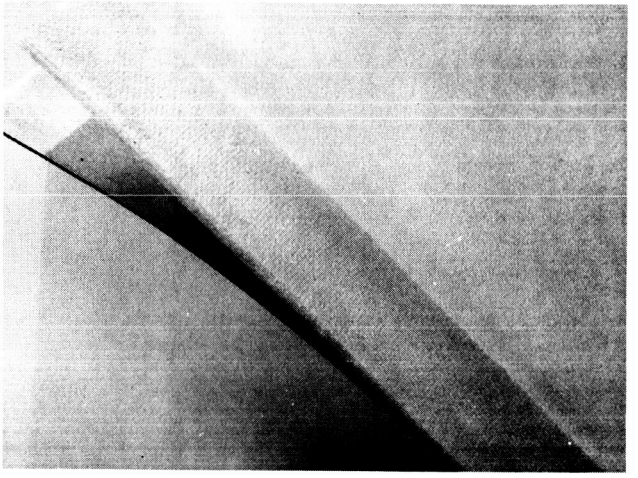
The tests previously discussed describing the material applied in bulk and reinforced with glass and ceramic fibers and also with 181 style glass fabric, were encouraging enough to warrant further efforts to increase bend resistance through glass fiber reinforcement. Subsequently, pre-preg techniques were devised and tested in the following way.

One set of bend specimens, designated Formulation Number 1 in Table II-III, was prepared by dissolving 50.0 gm. Kel-F 800 resin in 100.0 gm. methyl ethyl ketone and adding 12.5 gm. HC-912 primer concentrate. 181 style glass fabric was then impregnated with this solution and was air dried for 1/2 hour. A second coat was applied and after 15 minutes, while it was still tacky, six plies of the impregnated fabric were pressed together on newly etched aluminum strips previously primed with the hot melt primer. The specimens were then cured in an air-circulating oven for 24 hours at 32°C, then overnight at 65°C. All specimens successfully passed the bend test at 76°K and a representative specimen, after test, is shown in Figure II-4.

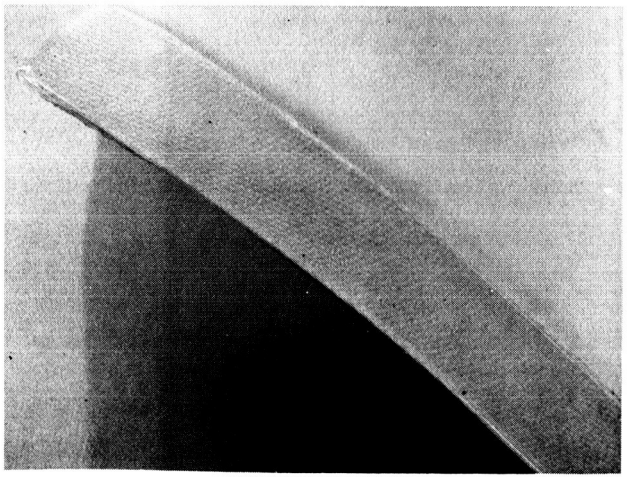
A second set of specimens, from Formulation Number 2 in Table II-III, was made in the same manner, except that three plies



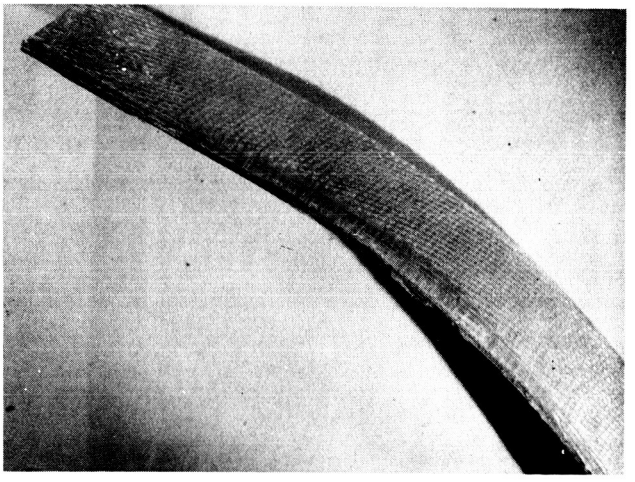
FN-1



FN-2

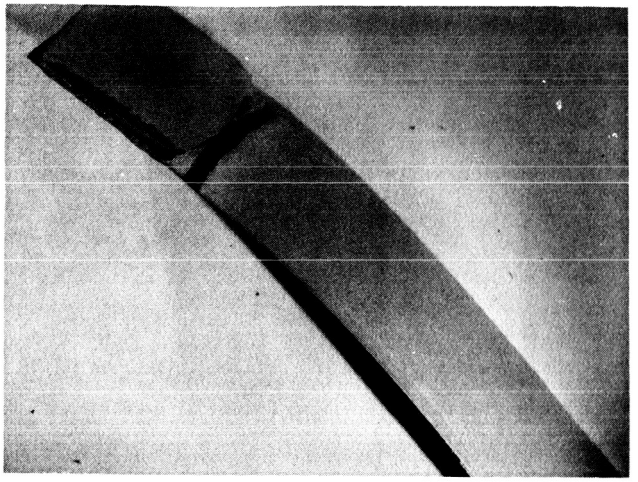


FN-3



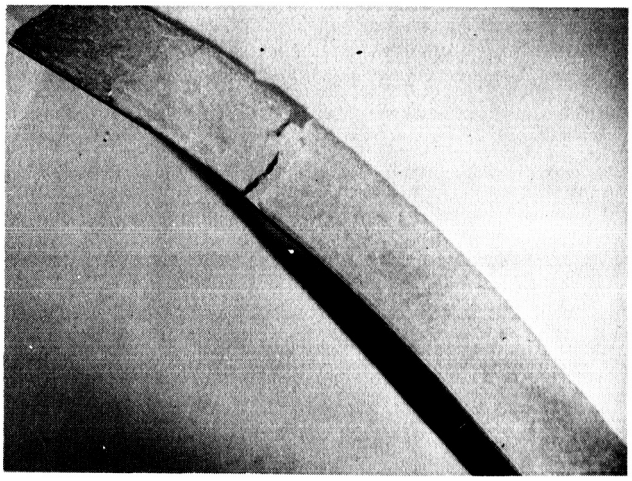
FN-4

Figure II-4. Specimens after bending at 76°K.



FN-5

FN-6



FN-7

Figure II-4. Specimens after bending at 76°K (continued).

were given three coats with a 1 hour air dry between each coat and the specimens were cured overnight at 80°C.

A third set of specimens, from Formulation Number 3 in Table II-III, was made using three plies air dried overnight, after each of three coatings was air dried 1/2 hour. The dry plies were made slightly tacky by heating with a heat gun and then were pressed together on newly etched and primed aluminum strips. Curing was again accomplished overnight at 80°C.

The fourth set of specimens, from Formulation Number 4 in Table II-III, was made in a similar manner. However, the HC-912 was omitted from the impregnating resin. The dry plies were again made slightly tacky before application by heating.

The results from these tests show the inherent flexibility at 76°K, of the Kel-F 800. All but Formulation Number 2 passed the bend test, with this material lacking the same degree of adhesion as the others. The reason for this lack of adhesion is not yet understood but may be due to attack on the primer by the residual solvents in the impregnating resin. An extensive drying of the plies was not accomplished here as in the later specimens.

Inclusion of the HC-912 in the resin is not required, as shown by the results of Formulation Number 4. Indeed, it is more desirable to remove the possibility of LOX instability due to small amounts of the HC-912 remaining in the cured resin.

The technique of using dry pre-preg techniques appears to offer a significant advantage in the use of this sealant. Not only was the problem of solvent removal (a limiting factor in a material's LOX stability) reduced, but field use may be simplified by supplying the user with impregnated glass fabric ready for use. A sample of Formulation Number 4 pre-preg has been given to NASA for LOX impact testing. In addition, tee peel specimens were made and tested to determine the degree of peeling adhesion at 76°K. The procedure and results are given in a subsequent part of this report section.

FN*	Composition	Amount	FN*	Composition	Amount
1	Kel-F 800 (dissolved in M.E.K.) HC-912 (21% solids) 6 plies 181 glass cloth Hot melt primer	50.0 g. 12.5 g.	5	Adiprene L-100 Castor oil Kel-F oil No. 3 Cab-O-Sil Chemlok 607 primer	12.5 g. 4.5 g. 8.5 g. 1.3 g.
2	Kel-F 800 (dissolved in M.E.K.) HC-912 (21% solids) 3 plies 181 glass cloth Hot melt primer	50.0 g. 12.5 g.	6	Adiprene L-100 Castor oil Kel-F oil No. 3 Cab-O-Sil 4 plies 181 glass cloth	12.5 g. 4.5 g. 8.5 g. 1.3 g.
3	Kel-F 800 (dissolved in M.E.K.) HC-912 (21% solids) 3 plies 181 glass cloth HC-912 concentrate primer	50.0 g. 12.5 g.	7	Adiprene L-100 Castor oil Kel-F oil No. 3 Cab-O-Sil Chemlok 607 primer	12.5 g. 4.5 g. 12.8 g. 1.5 g.
4	Kel-F 800 (dissolved in M.E.K.) 4 plies 181 glass cloth Hot melt primer	100.0 g.			

*FN = Formulation Number

Table II-III. Sealant modification formulations.

In the work reported on the development of cryogenic potting compounds[1] the addition of a LOX compatible filler to an Adiprene elastomer provided a composite that was LOX safe. Work, therefore, was undertaken to develop a LOX compatible sealant by the addition of Kel-F oils to the Adiprene L-100 castor oil sealant found previously to be serviceable at LOX temperature. Specimens were therefore prepared to determine the compatibility of the fluorocarbon oil with the polyurethane and to establish the strengths of such a plasticized system.

Bend test specimens, designated Formulation Numbers 5 and 6 in Table II-III, were made from the same basic system, except that FN-6 was reinforced with glass fabric. Formulation Number 7 was used to make bend test specimens using the maximum amount of Kel-F oil tolerated in the system. All specimens were cured 16 hours at 85°C.

The test results indicate the ability of this sealant to resist bending loads at 76°K when suitably reinforced. Pictures of representative specimens after testing are shown in Figure II-4.

Shortly after these tests were run, the Hughes Aircraft Company was directed by the Contracting Agency to refrain from further work on this approach because of the Contracting Agency's disagreement with conclusions of Reference 1. Although this did not appear to be a fruitful approach, samples of Formulation Number 7 were sent to NASA for LOX impact testing. This was done for the sake of completeness and to provide NASA with further evidence as to the LOX sensitivity of the material. These impact test results are given on page 19 of this section.

Samples of Kel-F 3700 gum stock were received and a sealant was compounded on a rubber mill using the following formulation:

Kel-F 3700	-	100 grams
zinc oxide	-	5 grams

1. R. J. Boot, C. B. Murphy, and O. L. Smith, "The Development of Potting Compounds for Cryogenic Application," Plastics Design and Processing, October 1962.

Dyphos (Dibasic lead phosphite, National Lead Co.)	-	5 grams
HMDA (hexamethylene diamine carbamate - 3 M Co.)	-	1.3 gram

Bend test specimens were made with this formulation using, in one case, Chemlok 607 primer and, in another, Kel-F 800 hot melt primer. In both instances, the test specimens failed the bend test at 76°K, exhibiting brittle failure. Also, because this material was a gum stock requiring fairly high curing temperatures and pressures, it was not considered usable under the scope of the contract.

PEEL TEST OF CANDIDATE LOX-SAFE SEALANT

In further evaluating the reinforced Kel-F 800 sealant, tee peel tests were made using Formulation Number 4. Four plies of 181 style glass fabric were used to bond two 0.020 x 1 x 12 inch etched and hot melt primed aluminum strips. They were then cured overnight at 100°C. Five specimens were tested at room temperature and five were tested at 76°K. The results are given in Table II-IV.

The results indicated that this material resisted the thermal shock without failing and that acceptable peel strength values are maintained at 76°K. Although the values reported in Table II-IV show the initial, high, and low values of each test, these figures may be misleading. The initial and high values in each instance are the same and one may conclude that after the initial break the peel strengths dropped to zero. This was not the case, however, and the average values were maintained at a finite figure above zero. Typical "steady" values, at 76°K, averaged between 2 and 3 lb./in.

Representative specimens, after test, are shown in Figure II-5.

IMPACT TEST OF CANDIDATE LOX-SAFE SEALANTS

Samples of the following materials were sent to NASA for LOX impact testing. The tests were conducted in accordance with MSFC-SPEC-106, titled "Compatibility of Materials for Liquid Oxygen Systems."

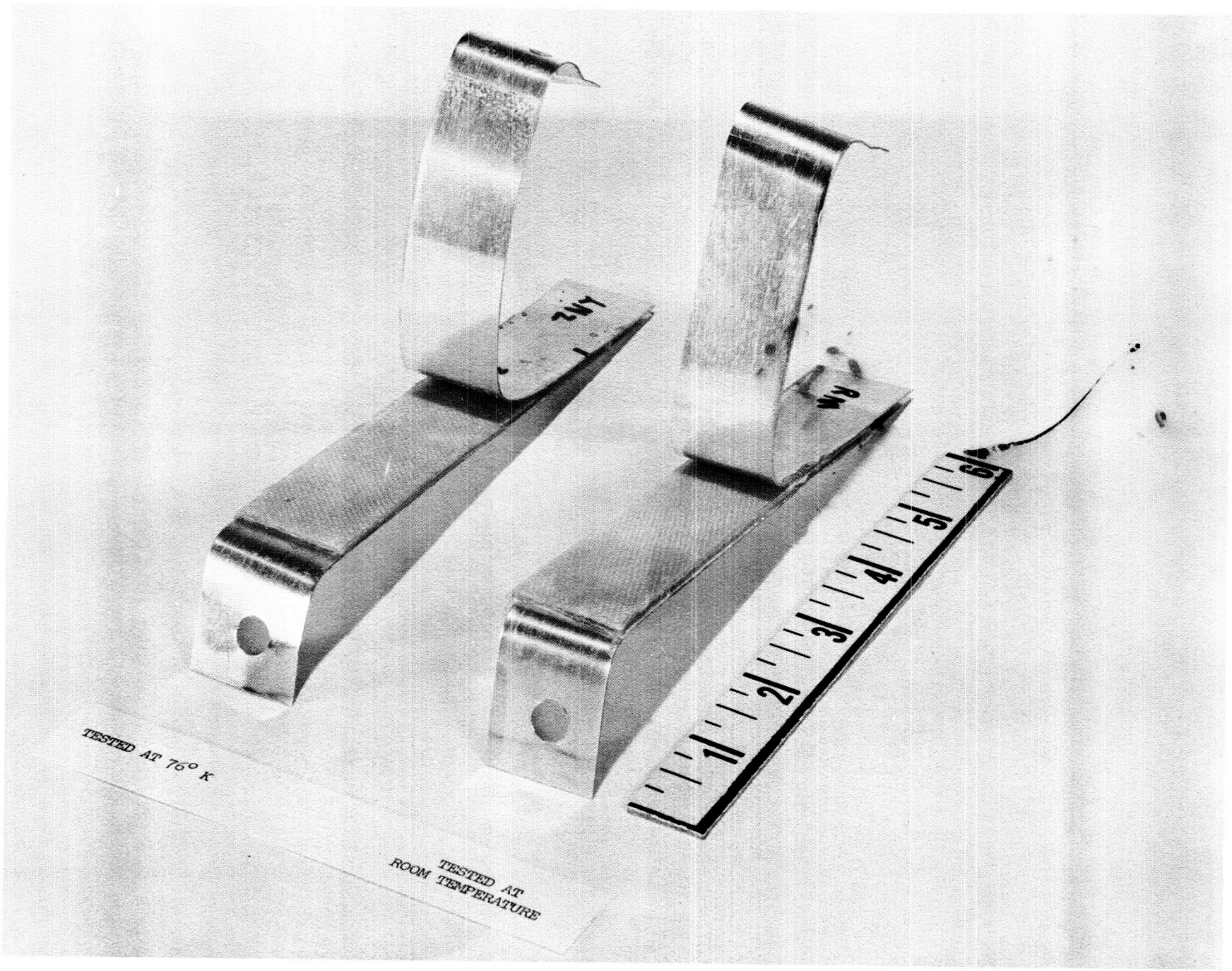


Figure II-5. Peel test specimens - glass reinforced Kel-F 800.

Specimen No.	Peel Strength (lb/in)			Failure		Test Temperature
	Initial	High	Low	Adh.	Coh.	
1	48.4	48.4	0.0	X		Room Temp.
2	8.2	8.2	0.0	X		Room Temp.
3	6.7	6.7	1.0	X		Room Temp.
4	1.8	1.8	0.3	X		Room Temp.
5	30.0	30.0	0.0	X		Room Temp.
6	19.7	19.7	0.0	X		76°K.
7	8.9	8.9	0.0	X		76°K.
8	13.0	13.0	0.0	X		76°K.
9	10.7	10.7	0.0	X		76°K.
10	11.7	11.7	0.0	X		76°K.
11	*	*	*			76°K.
*Failed in grips						

Table II-IV. Tee peel tests - Kel-F 800 Formula No. 4.

Compositions of the specimens and results of the tests are as follows:

Material	Impact Energy ft-lbs	No. Reactions/ No. Tests
Kel-F Hot-Melt Primer	72.3	2/7
	36.15	1/2
	21.69	1/3
	7.23	0/8
Kel-F 800-Impregnated Glass Cloth	72.3	3/4
	36.15	0/16
Polyurethane-Kel-F Impregnated Glass Cloth	72.3	2/2
	36.15	2/2
	21.69	2/2
	7.23	0/14

As these sensitivity levels are excessive to minimum NASA requirements, the compositions involved were disapproved for use in LOX systems.

As the sensitivity may be attributed, in part, to solvent entrapped in the hot-melt primer, NASA recommended that additional work with the Kel-F 800 hot-melt primer include investigations of other solvents, such as trichloroethylene and a lightweight chlorofluorocarbon oil, in efforts to reduce the sensitivity levels.

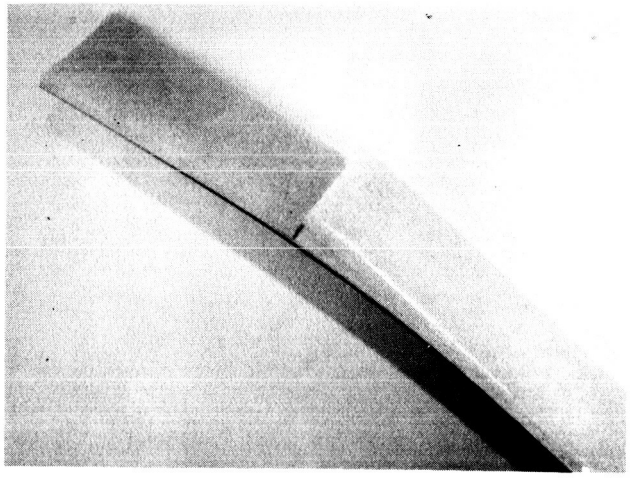
However, the scope of work for the third year's effort has been modified to emphasize synthesizing of new polymers for cryogenic sealant use regardless of LOX-sensitivity. Therefore, a continuation of LOX-Safe sealant development using these new techniques has been shelved.

CANDIDATE SEALANTS FOR NON-LOX APPLICATIONS

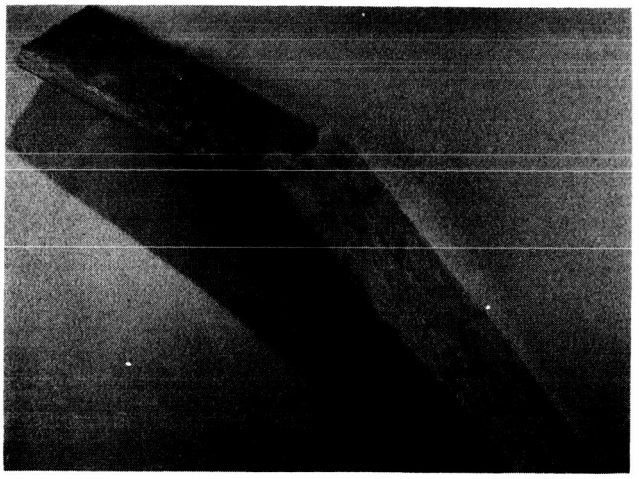
For non-LOX applications, sealants based upon the existing Adiprene L-100, castor oil system, and upon a newly synthesized silicone polymer, were tested to show their resistance to bending at 76°K. Formulas are shown in Table II-V and representative specimens are shown in Figure II-6.

Fiberfrax washed fibers and asbestos were used in the Adiprene formulations in further attempts to provide reinforcement of good load carrying properties that will give an overall sealant coefficient of thermal expansion approximating that of aluminum. Such reinforcements in the resin before application would be more conveniently used than the present glass fabric reinforced system. Neither formula appears promising, even though the Fiberfrax wets easier and provides a sealant viscosity lower than the glass fiber formula.

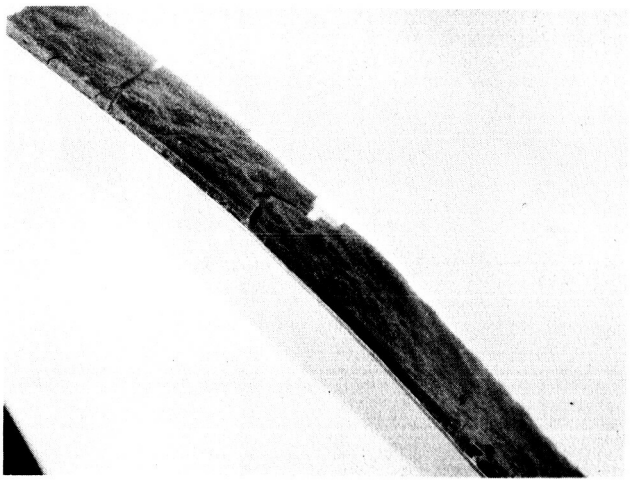
The sealant bend specimens (see Table II-V) were screened using: (1) Adiprene L-100, castor oil and fiberfrax washed fibers, (2) Adiprene L-100, castor oil and asbestos filler and (3) Polybutylmethylsiloxane polymers previously prepared in the laboratory. The small amount of polybutylmethylsiloxane (shown in Table II-V, FN-3) was intended to provide a silicone having the properties of non-crystallinity and still maintaining the inherent low temperature properties of a dimethyl silicone. However, the synthesized polymer exhibited brittle



FN-1



FN-2



FN-3

Figure II-6. Photographs of bend test specimens.

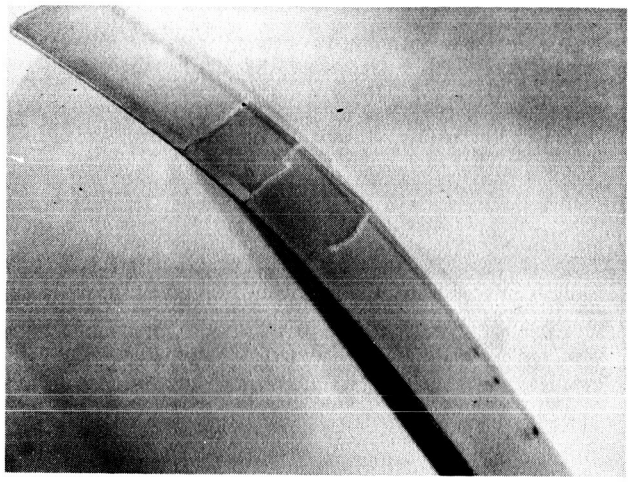
FN*	Composition	Amount	FN*	Composition	Amount
1	Adiprene L-100	100.0 g.	3	Polybutylmethylsiloxane	7.5 g.
	Castor oil	36.0 g.		Polydimethylsiloxane	92.5 g.
	Fiberfrax (washed)fibers	50.0 g.		Cab-O-Sil	2.0 g.
	Chemlok 607 primer			Benzoylperoxide	1.6 g.
2	Adiprene L-100	100.0 g.		Chemlok 607 primer	
	Castor oil	36.0 g.			
	Asbestos, medium grade, acid washed	50.0 g.			
	Chemlok 607 primer				

*FN = Formulation Number

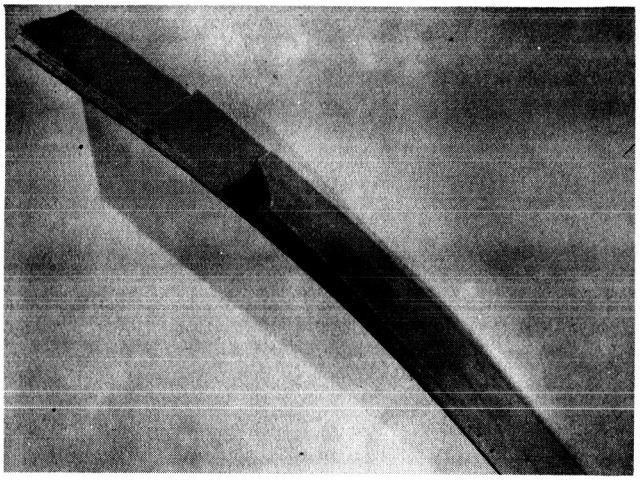
Table II-V.

failure and shows no improved low temperature flexibility over a straight dimethyl silicone at 76°K. Formulation numbers 1 and 2 also failed as shown in Figure II-6.

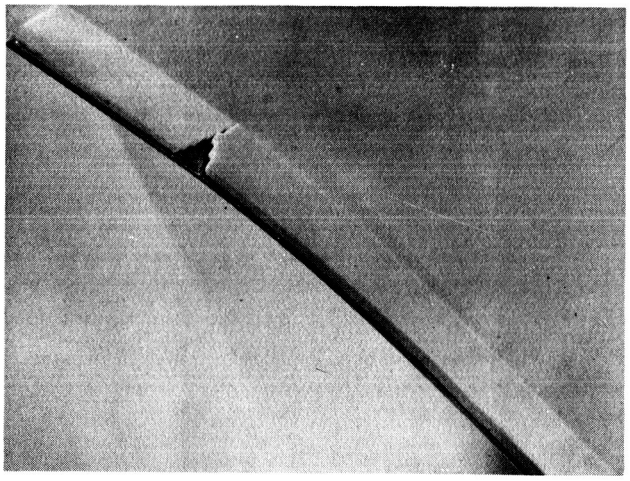
Therefore, the search for existing materials was continued. Sealants which were obtained from commercial sources and subjected to the low temperature flexibility test at 76°K, are listed in Table II-VI. The procedure for subjecting materials to flexibility test was described earlier in this report. Photographs of specimens are shown in Figure II-7. All of the materials failed the screening test either by brittle failure or by cracking. Two of the products showed enough promise to warrant further testing after modification. A polyurethane resin of the Adiprene type, designated ECD-420, was reported by duPont to retain a greater degree of flexibility than Adiprene L-100 at temperatures down to -65°F (219°K). The other material that warranted further testing was General Electric's experimental silicone rubber, RTV-X511.



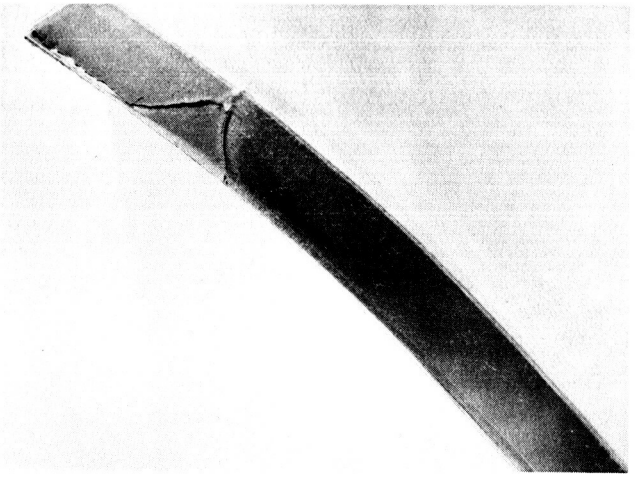
FN-1



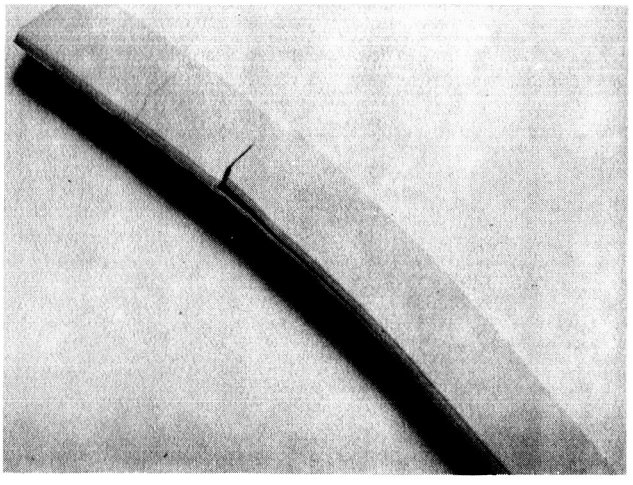
FN-2



FN-3



FN-4



FN-5

Figure II-7. Low temperature flexibility test - new sealants.

The existing sealants which showed promise in the low temperature flexibility test were modified by compounding with various reinforcing fillers or curing agents or by changing the primer. The modifications are detailed in Table II-VII. Photographs of the specimens after modification and application of the low temperature flexibility test are shown in Figure II-8.

Curved copper metal fibers were incorporated in the Adiprene L-100 plus castor oil system (Table II-VII, FN-1) in an attempt to provide a filler system that would be contained in the resin before sealant application. Since the fibers are curved, it was hoped that they would provide an interlocking lattice which would give reinforcing continuity throughout the sealant. However, these fibers did not furnish sufficient reinforcement as the specimen failed the flexibility test. Aluminum was added to this same Adiprene L-100 plus castor oil system (FN-2), but it too failed to provide sufficient reinforcement. Using a somewhat different approach, the Adiprene L-100 foam (FN-3), prepared according to one of the foamed-in-place crevice sealant formulas, also fractured in the flexibility test.

It was found that ECD-420 reinforced with milled glass fibers (FN-4) or 181 glass cloth (FN-5) did not perform as well as the standard Adiprene L-100 at temperatures down to -65°F (219°K). The ECD-420 material was dropped from further consideration.

One sealant modification that has shown promise is the reinforcement with 181 glass cloth of General Electric RTV-X511 silicone rubber (FN-6). This material did pass the flexibility test at 76°K and was carried on for further evaluation.

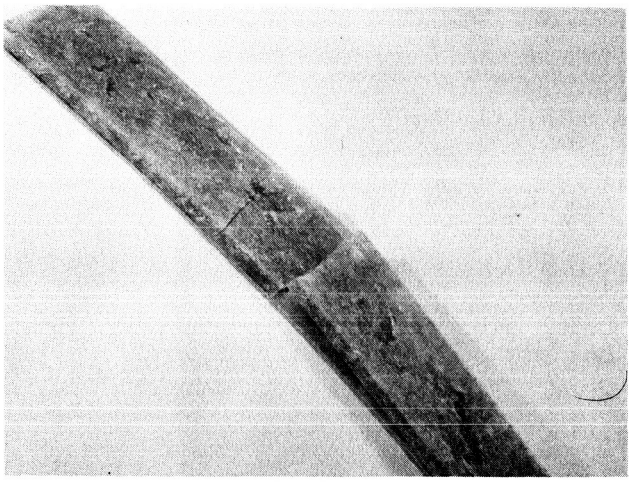
Bend test specimens were prepared and tested at 76°K with another experimental silicone sealant manufactured by General Electric Co. This sealant, designated RTV-X560, is similar to the RTV-X511 that was considered (along with the Adiprene L-100 castor oil sealant) as the best candidate sealant for non-LOX use down to 20°K. The RTV-X560 specimens reinforced with glass fabric passed the bend test, and pictures of representative specimens after test are shown in Figure II-9. The formulations are given in Table II-VIII. The RTV-X511 and

RTV-X560 are chemically similar, having bulky side groups on the siloxane backbone. This renders them incapable of crystallization during the expected cooling conditions, as shown in the thermal contraction studies of this report. The results of vibration tests on RTV-X511 silicone sealant is also given in a later section of this report.

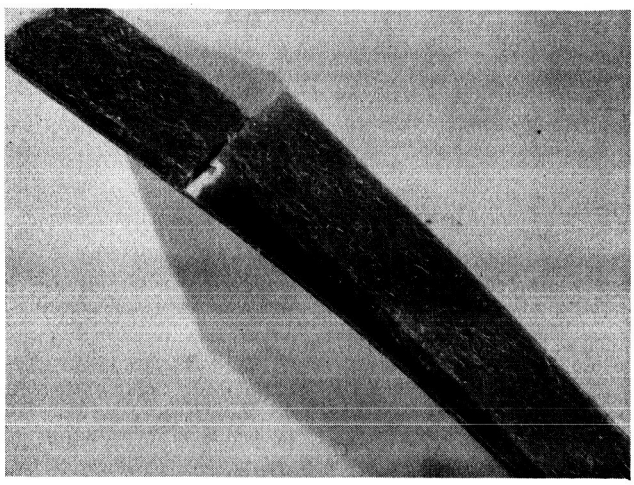
FN*	Product Designation	Product Type
1	DuPont ECD-420 cured with castor oil Chemlok 607 primer	Polyurethane
2	Dow Corning Q-2-0103 Dow Corning QA-2-1011 primer	Silicone
3	Products Research PR-1540 Products Research PR-1531 primer	Polyurethane
4	Products Research PR-1536 Products Research PR-1531 primer	Polyurethane
5	GE RTV-X511 Dow Corning QA-2-1011 primer	Silicone

*FN = Formulation Number

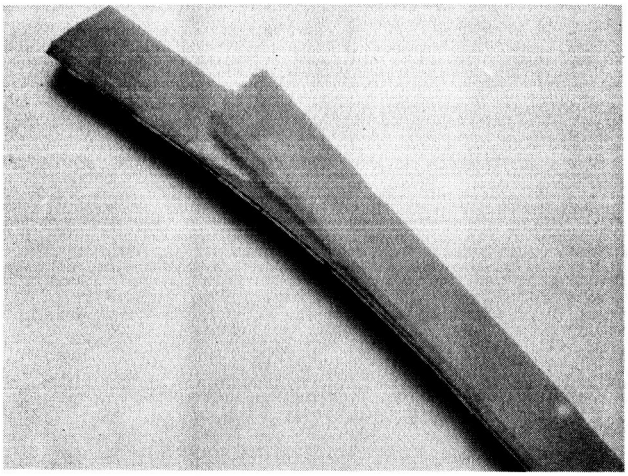
Table II-VI. New sealants screened.



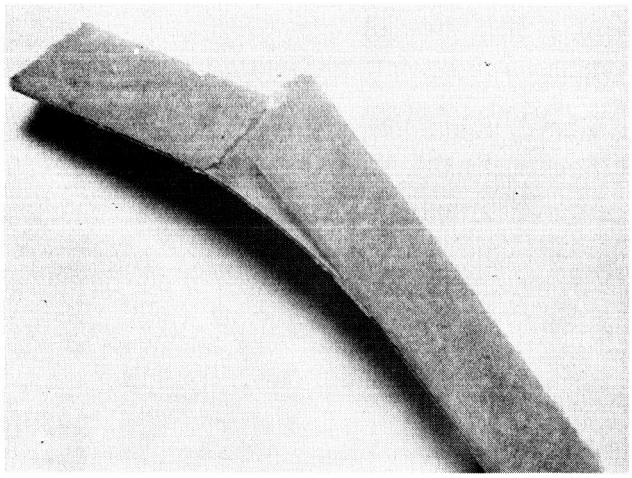
FN-1



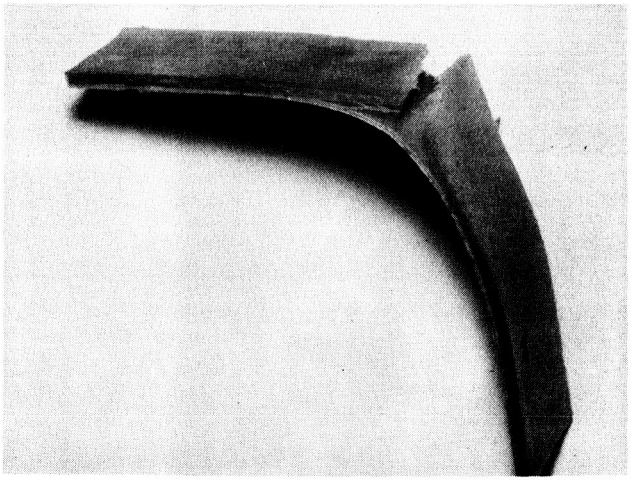
FN-2



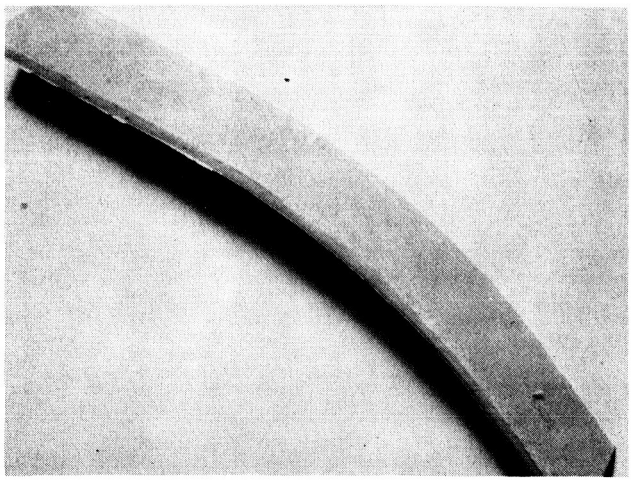
FN-3



FN-4

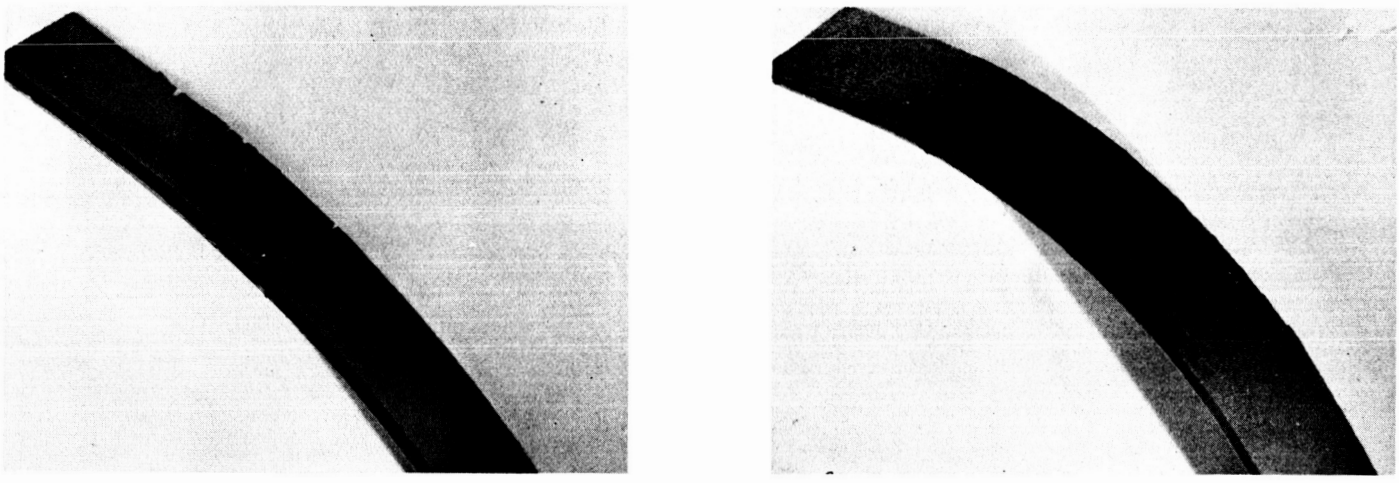


FN-5



FN-6

Figure II-8. Low temperature flexibility test - modifications.



FN-1 FN-2

Figure II-9. Specimens after bending at 76°K.

FN*	Composition	Amount	FN*	Composition	Amount
1	Adiprene L-100	100.0 g.	4	ECD 420	100.0 g.
	Castor oil	36.0 g.		Castor oil	25.0 g.
	Fiberfrax (washed) fibers	25.0 g.		Milled glass fibers	23.5 g.
	Copper fibers, curved	25.0 g.		Chemlok 607 primer	
2	Adiprene L-100	100.0 g.	5	ECD 420	100.0 g.
	Castor oil	36.0 g.		Castor oil	25.0 g.
	Fiberfrax (washed) fibers	25.0 g.		181 glass cloth - 6 plies	
	Aluminum wool	29.0 g.		Chemlok 607 primer	
	Chemlok 607 primer				
3	Adiprene L-100	100.0 g.	6	RTV-X511	100.0 g.
	MOCA (curing agent)	9.7 g.		Thermolite 12 catalyst	0.5 g.
	DABCO (catalyst)	0.2 g.		181 glass cloth - 6 plies	
	XF-1034 (surfactant)	2.0 g.		Q A-2-1011 primer	
	Water	0.2 g.			
	Milled glass fibers	31.6 g.			
	Chemlok 607 primer				
	Foam formed on the aluminum strip				

*FN = Formulation Number

Table II-VII. Sealant modification formulations.

FN*	Composition	FN*	Composition
1	RTV-X560 Silicone rubber Thermolite 12 Catalyst QA-21011 primer	2	RTV-X560 Silicone rubber T-12 catalyst 4 plies 181 glass cloth QA-21011 primer
*FN = Formulation Number			

Table II-VIII. Sealant modification formulations.

III. NEW CANDIDATE POLYMER SYSTEMS

SYNTHESIS OF NEW POLYMERS

Because it is important to have a cryogenic sealant which is insensitive to liquid oxygen, synthesis of fluorinated materials was considered. Fluorinated polymers, such as Teflon and Kel-F, are insensitive to liquid oxygen; however, it is difficult to bond them to metal surfaces. This is because they consist of repeating difluoromethylene or fluorochloromethylene groups which do not have much adhesive power. Furthermore, their structure is such that there is no simple method of curing them after application to metal surfaces.

In order to make a fluorinated polymer containing functional groups which can be used for curing processes, condensation of fluorinated dicarboxylic acids and fluorinated glycols to the corresponding polyesters was attempted.

The compounds hexafluoroglutaric acid and 2,2,3,3,4,4-hexafluoro-1,5-pentanediol are commercially available. These two compounds have been used to prepare a fluorinated polyester by the following reaction:

$$n\ HO_2CCF_2CF_2CF_2CO_2H + n\ HOCH_2CF_2CF_2CF_2CH_2OH \rightarrow$$

$$HO\left(\overset{O}{\overset{\|}{C}}CF_2CF_2CF_2\overset{O}{\overset{\|}{C}} - OCH_2CF_2CF_2CF_2CH_2O\right)_nH + (2n-1)\ H_2O$$

The reaction was carried out by refluxing a solution of the two compounds in xylene and collecting the water produced by the condensation. Benzene was not satisfactory as a solvent for the reaction because the compounds would not dissolve completely in it. The condensations in xylene produced approximately half the amount of water theoretically possible, even when acid catalysts such as p-toluenesulfonic acid and sulfuric acid were incorporated. The condensation reaction did not proceed further because the product precipitated from the reaction mixture at this point. The fluorinated polyester was isolated but could not be

purified further, since no common laboratory solvent was found which would dissolve the material. The product was a granular solid with a slightly waxy surface. It did not melt on heating, but changed to a black solid. Heat and pressure had very little effect since the product did not change when kept under 50,000 psi pressure at 200°C for a few hours.

Since the condensation did not yield the theoretical amount of water, preparation of the fluorinated polyester was attempted by the following procedure:

$$HO_2CCF_2CF_2CF_2CO_2H + 2SOCl_2 \rightarrow ClC(=O)CF_2CF_2CF_2C(=O)Cl$$

$$n\ ClC(=O)CF_2CF_2CF_2C(=O)Cl + n\ HOCH_2CF_2CF_2CF_2CH_2OH \xrightarrow{H_2O}$$

$$HO\left(-C(=O)CF_2CF_2CF_2C(=O)-OCH_2CF_2CF_2CF_2CH_2O-\right)_n H$$

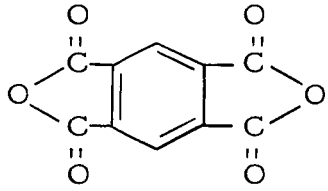
The hexafluoroglutaric acid was refluxed with an excess of thionyl chloride for some time, and then the unreacted thionyl chloride was removed by distillation under vacuum. Surprisingly, the whole reaction mixture distilled, leaving no residual product. The reaction was repeated with the same result. Apparently the hexafluoroglutaryl chloride formed and then decomposed into volatile materials. Consequently, the polyester could not be synthesized in this way.

Curing of the fluorinated polyester is made possible by the presence of terminal hydroxyl and/or carboxyl groups on the polymer chains, and by the possibility of ester interchange with tri- or tetra-substituted carboxylic acids and alcohols. Because the fluorinated polyester was not soluble, curing experiments were first carried out on a similar unfluorinated polyester made from adipic acid and 1,5-pentanediol:

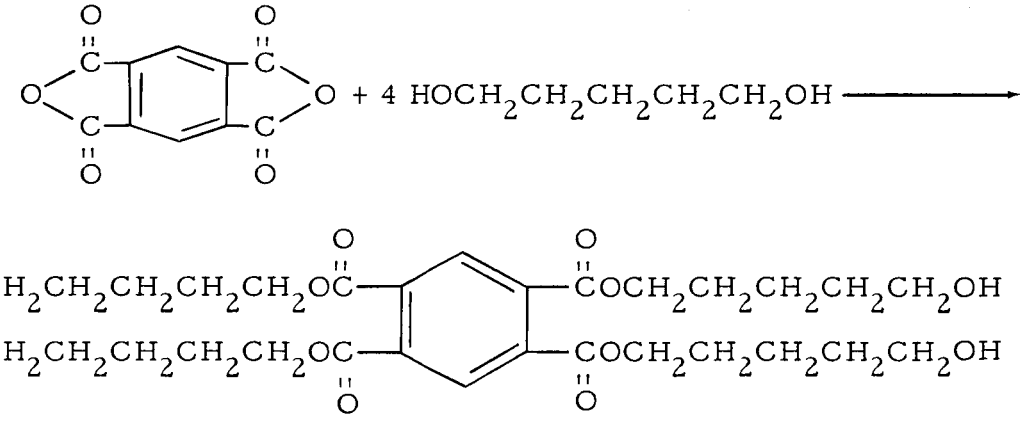
$$n\ HO_2CCH_2CH_2CH_2CH_2CO_2H + n\ HOCH_2CH_2CH_2CH_2CH_2OH \rightarrow$$

$$HO\left(\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}} - OCH_2CH_2CH_2CH_2CH_2O\right)_n H + (2n-1)\ H_2O$$

In one experiment, this polyester was treated with pyromellitic dianhydride, the anhydride of a benzenetetracarboxylic acid:



The product was at least partially cured, since it was tougher and more viscous than the original polyester. In another experiment, the condensation to the polyester was carried out in the presence of pyromellitic dianhydride, the pyromellitic dianhydride replacing some of the adipic acid in the condensation mixture. Again a very viscous polymer was obtained, indicating that the pyromellitic dianhydride had partially cured the polyester. In a third experiment, a hydroxyl-terminated prepolymer was prepared from pyromellitic dianhydride and 1,5-pentanediol:



This prepolymer was then treated with adipic acid and more 1,5-pentanediol. A tacky gum resulted.

Since the fluorinated polyester was not soluble in any solvent, an ester condensation was carried out with a mixture of two parts of hexafluoroglutaric acid and three parts of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol in an attempt to obtain a low-molecular-weight hydroxyl-terminated prepolymer which could be treated further with pyromellitic dianhydride. The product was as intractable as the fluorinated polyester previously obtained, with less than the theoretical amount of water formed as before. Since the product was insoluble in solvents, it was mixed with pyromellitic dianhydride and heated without solvent at 260 to 300°C for eight hours. There was no significant reaction.

In another condensation, the fluorinated monomers were combined with pyromellitic dianhydride and the condensation was then carried out. As before, only about half of the theoretical amount of water had been collected when the product separated from the reaction mixture. Continued refluxing did not result in the formation of any more water. The product was a white solid which did not seem usable as a sealant.

The fluorinated polyester was treated with several other materials which can react with terminal hydroxyl or carboxyl groups in an attempt to cure it. Portions of the solid polyester were heated at 190°C with

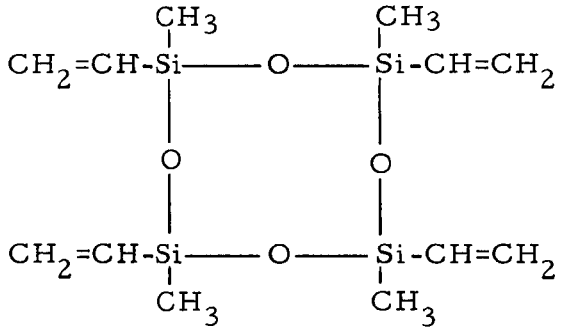
(1) N,N'-dicinnamylidene-1,6-hexanediamine
(2) glycerol
(3) dicumyl peroxide
(4) phenyltrichlorosilane
(5) diphenylmethane-4,4'-diisocyanate

for three days, but, other than decomposition of the curing agent and some discoloration, there was no evidence of reaction. Further work with the fluorinated polyester was stopped.

The work on polybutylmethylsiloxanes, discussed in the Final Report of the first year, was continued. Because of the difficulty encountered in curing the polymethylbutylsiloxanes, vinyl groups were

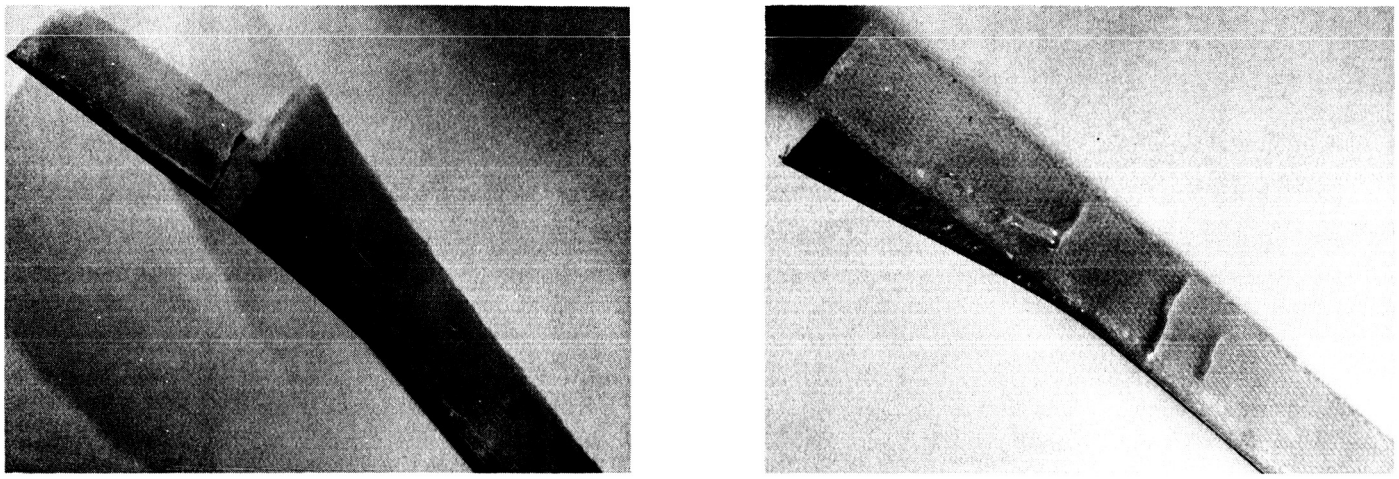
incorporated into the polymers along the siloxane chain. This was accomplished by catalytic equilibration of mixtures of tetravinyltetramethylcyclotetrasiloxane, tetrabutyltetramethylcyclotetrasiloxane, and octamethylcyclotetrasiloxane. The 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane was prepared by acid hydrolysis of vinylmethyldiethoxysilane as shown in the following equation:

$$4\,(CH_2{=}CH)(CH_3)Si(OC_2H_5)_2 \xrightarrow{HCl,\,H_2O}$$



The product obtained was actually a mixture of cyclic tetramer, pentamer, and hexamer; for the purpose of the equilibrations, it was assumed to be all cyclic tetramer.

Because of its ready availability, a 25 percent aqueous solution of tetramethylammonium hydroxide was tried as an equilibration catalyst, but the resultant polymers did not have as high a molecular weight as obtained previously. A fresh solution of 25 percent aqueous tetramethylammonium hydroxide was dehydrated under vacuum with very slight warming to give solid tetramethylammonium hydroxide (contaminated with a little of the corresponding carbonate and some water). This solid catalyst gave good polymers, but decomposition of the catalyst by heating above 150°C after the equilibration leaves trimethylamine in the polymer. Trimethylamine is known to cause rapid decomposition of the peroxides used as curing catalysts; hence, the quaternary ammonium hydroxide was discarded as an equilibration catalyst.



FN-1 FN-2

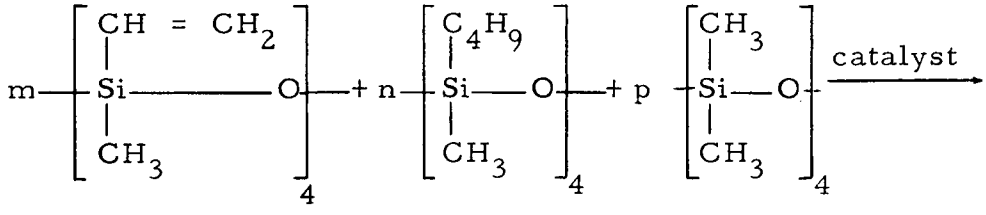
Figure III-1. Low temperature flexibility test - synthesized resins.

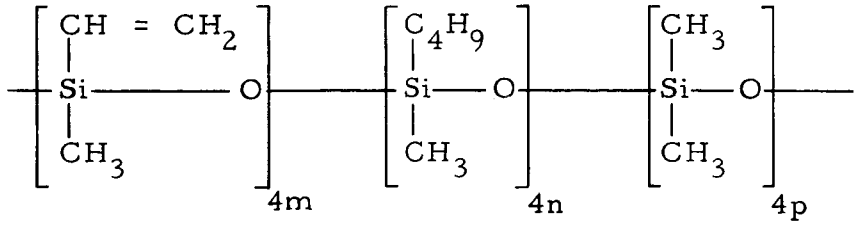
Use of tetra-n-butylphosphonium silanolate catalyst, mentioned in the first year Final Report, was discontinued, because the catalyst solution was not stable. The siloxane solvent polymerized at room temperature to a point where it was too viscous for use.

The equilibration catalyst of choice is now an aqueous solution of tetra-n-butylphosphonium hydroxide. It is made from tri-n-butylphosphine as previously described. The catalyst is added at 110 - 120°C to the cyclosiloxane mixture to be equilibrated, and the removal of water is speeded by blowing nitrogen gas over the surface of the mixture for several minutes. Unfortunately, the equilibrations are not consistently successful. Difficulty arises in scaled-up experiments, probably because the extra water added with the catalyst to the larger reaction mixture must be removed. Occasionally the mixture of cyclosiloxanes does not equilibrate, or requires the addition of more catalyst before significant reaction takes place.

Two different mixtures of cyclosiloxanes were converted by equilibration to polysiloxanes with random alkyl side-groups attached to the silicon atoms. The two equilibrations were carried out for two hours at about 115°C, using aqueous tetra-n-butylphosphonium hydroxide as a catalyst. The resulting siloxanes had the following alkyl group composition:

	B4200-4	B4200-7
Vinyl	1.12 mole%	1.16 mole%
Butyl	3.32 mole%	6.90 mole%
Methyl	95.6 mole%	91.9 mole%





It was found that the resulting polymers could be cured easily by dicumyl peroxide on heating at 100°C for several hours. However, curing is inhibited by air, so the polymer samples are either covered in the oven or cured in a vacuum oven. Other curing catalysts were tried (dibutyltin dilaurate, 50 percent benzoyl peroxide in silicone oil, p-cumyl hydroperoxide, GE 720-28-13B) but showed no advantage over dicumyl peroxide and were occasionally not as good. The first resin (B4200-4) was reinforced with glass fibers and with 181 glass cloth and cured with dicumyl peroxide on standard primed aluminum strips. A full cure throughout the material was obtained by placing a cellophane film on the sample surface. The compositions are shown below:

1.	Polysiloxane B4200-4	24.0 g.
	Dicumyl peroxide	1.2 g.
	Milled glass fibers	10.8 g.
	(G. E. XS-4004 primer)	
2.	Polysiloxane B4200-4	24.0 g.
	Dicumyl peroxide	1.2 g.
	181 Glass cloth - 2 plies	
	(D. C. QA-2-1011 primer)	

Photographs of the specimens after application of the low temperature flexibility test are shown in Figure III-1. The first specimen adhered to the aluminum substrate, but failed the test. The second specimen peeled from the substrate, and also developed cracks.

A specimen made from resin B4200-7 shrank after curing and could not be tested.

EXPERIMENTAL

Poly(2,2,3,3,4,4-hexafluoropentamethylene hexafluoroglutarate) (B4200-9)

A mixture of 4.24 g. of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol and 4.80 g. of hexafluoroglutaric acid in 50 ml. of dry xylene was refluxed for 23 hours, during which time approximately 0.5 ml. of water was collected. A white precipitate separated. The mixture was

filtered hot with suction, and the white solid was washed with benzene and air-dried. It was insoluble in alcohols (methanol, ethanol), in ketones (acetone, butanone), in esters (ethyl acetate, methylcellosolve acetate), in ethers (diethylene glycol diethyl ether), in chloroform, N,N-dimethylformamide, and other solvents. The solid did not melt, but turned black when heated.

Hexafluoroglutaryl Chloride (B4200-23)

A mixture of 7.2 g. of hexafluoroglutaric acid and 8.73 ml. of thionyl chloride (freshly distilled) was refluxed 93.5 hours. The mixture was then distilled at about 25 torr. Everything distilled. The same reaction was carried out by refluxing for 22 hours. Again, there was no product remaining after the preliminary vacuum distillation.

Poly(pentamethylene adipate) (B4200-13)

A mixture of 10.4 g. of 1,5-pentanediol and 14.6 g. of adipic acid in 50 ml. of dry xylene was refluxed 18 hours. The theoretical amount of water was collected. Evaporation of the xylene left a very thick oil, which became semi-solid after several days.

Some of this ester (from 3.5 g. of 1,5-pentanediol and 4.9 g. of adipic acid) was heated with 0.36 g. of pyromellitic dianhydride in xylene for 17 hours. The solvent was then removed, leaving a resin which was tougher than the uncured poly(pentamethylene adipate).

A mixture of 6.6 g. of adipic acid, 0.55 g. of pyromellitic dianhydride, and 5.2 g. of 1,5-pentanediol was refluxed 16 hours. The theoretical amount of water was collected. Evaporation of the solvent left a resin similar to that above obtained by treating the polyester with pyromellitic anhydride.

A mixture of 16.7 g. of 1,5-pentanediol and 4.4 g. of pyromellitic dianhydride in 50 ml. of dry xylene was refluxed overnight. To the mixture was added 25.0 g. of 1,5-pentanediol and 52.6 g. of adipic acid and refluxing was continued over the weekend. The reaction mixture was quite thick and somewhat gelatinous. The solvent was removed by heating under vacuum, leaving a slightly tacky gum.

Condensation of 2,2,3,3,4,4-Hexafluoro-1,5-pentanediol, Hexafluoroglutaric Acid, and Pyromellitic Dianhydride (B4200-16)

A mixture of 4.24 g. of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, 4.32 g. of hexafluoroglutaric acid, and 0.22 g. of pyromellitic dianhydride in 50 ml. of dry xylene was refluxed 40 hours. The reaction mixture had two phases at the start. During the first overnight period of heating the second liquid phase disappeared, a white solid separated, and 0.38 ml. of water was collected (theoretical = 0.72 ml.). No further water formed after this. The solid was filtered with suction, and washed with xylene and benzene. It was a white granular substance insoluble in all the solvents.

Curing Experiments with Poly(2,2,3,3,4,4-hexafluoropentamethylene hexafluoroglutarate) (B4200-22)

In other curing experiments 830 mg. of fluorinated polyester was mixed with the following amounts of material in test tubes and heated in a bath at 190°C for 69 hours. The results are given after each curing agent.

(1) 50 mg. of N,N'-dicinnamylidene-1,6-hexanediamine (Du Pont, Diak #3); discolored granular product.
(2) 37 mg. of glycerol; slightly discolored granular product.
(3) 246 mg. of dicumyl peroxide; dark brown, mostly granular, a few tarry spots.
(4) 211 mg. of phenyltrichlorosilane; tan-colored granular product which did not react with water after excess phenyltrichlorosilane was removed.
(5) 250 mg. of diphenylmethane-4,4'-diisocyanate (Nacconate 300); dark granular solid with a few tarry spots.

1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (B4018-54)

A mixture of 1150 g. of redistilled vinylmethyldiethoxysilane and 1150 ml. of 6 N hydrochloric acid was refluxed for 72 hours. The organic phase was separated, washed four times with water, dried over anhydrous potassium carbonate, treated with 5 g. of

p-tert-butylcatechol (as antioxidant) and distilled under reduced pressure through a Vigreux column. The distillate, again treated with p-tert-butylcatechol, was redistilled through the Vigreux column. The fraction distilling at 90°-118°C at 2-1/2 torr was collected. The crystals of p-tert-butylcatechol in this fraction were filtered off, leaving 210 g. (34 percent yield) of a mixture of various vinylmethylcyclosiloxanes, probably from the cyclotetrasiloxane through the cyclohexasiloxane.

Poly(vinylbutylmethylsiloxane) (B4200-4)

A solution was prepared by mixing 5 g. (0.0145 mole) of 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, 20 g. (0.0430 mole) of 1,3,5,7-tetrabutyl-1,3,5,7-tetramethylcyclotetrasiloxane, and 175 g. (0.590 mole) of octamethylcyclotetrasiloxane. This mixture contains 1.12 mole percent vinyl groups, 3.32 mole percent butyl groups, and 95.6 mole percent methyl groups. The solution, in a 250 ml. Erlenmeyer flask, was heated to 110°C in an oil bath. Nitrogen was passed over the surface of the solution and 40 drops of aqueous tetra-n-butylphosphonium hydroxide was added. The flow of nitrogen was continued for several minutes until the aqueous phase had disappeared. The flask was then closed with a drying tube and heated at 110 - 120° for two hours. After cooling, some of the thickened polymer was mixed with 3 percent pulverized dicumyl peroxide and cured overnight in an oven at 100°C. Curing of the portion of the polymer exposed to air was inhibited, but the lower unexposed portion was cured. Covering the polymer during the heating period resulted in a fully-cured elastomer.

IV. PHYSICAL PROPERTY TESTING OF CANDIDATE MATERIALS

To verify the acceptability of a sealant for cryogenic applications, tests of critical physical properties must be made. This section reports contraction studies of RTV X-511 and B4200-4 Poly (methylbutylvinylsiloxane); vibration tests of RTV X-511, Kel-F800, and Adiprene L-100 cured with castor oil; and shock tests of Adiprene L-100 cured with castor oil.

THERMAL CONTRACTION STUDIES

The thermal contraction characteristics and volume changes of RTV X-511 and synthesized B4200-4 Poly (methylbutylvinylsiloxane), previously reported, were observed during cooling to 76°K. The apparatus used is shown in Figure IV-1. Volume changes at transition temperatures should, ideally, be held to a minimum; and the coefficients of thermal contraction should match those of the metal substrates as closely as possible.

Cylindrical specimens approximately 3 inches long and 1/2 inch in diameter, were placed in a quartz tube suspended in a Dewar flask. A thin quartz rod, resting on the specimens, protruded above the tube. A cathetometer was used to measure the change in height of the rod and, thus, the contraction of the specimens. A bath of n-propanol, cooled by the addition of liquid nitrogen, was used. After each addition, the temperature of a copper-constantan thermocouple imbedded in the specimen was noted. The length measurements were made after the specimen temperature had stabilized for 15 minutes. The bath was only useful down to approximately 170°K. Near this temperature the tests were interrupted and liquid nitrogen was substituted for the bath and the final point was taken at 76°K. For comparison, the contraction was measured in a direct run by rapid cooling to 76°K.

The curves plotted for these two materials are shown in Figures IV-2 and IV-3. Both show a lack of crystallization in this temperature range. The coefficients of thermal expansion (contraction) are rather

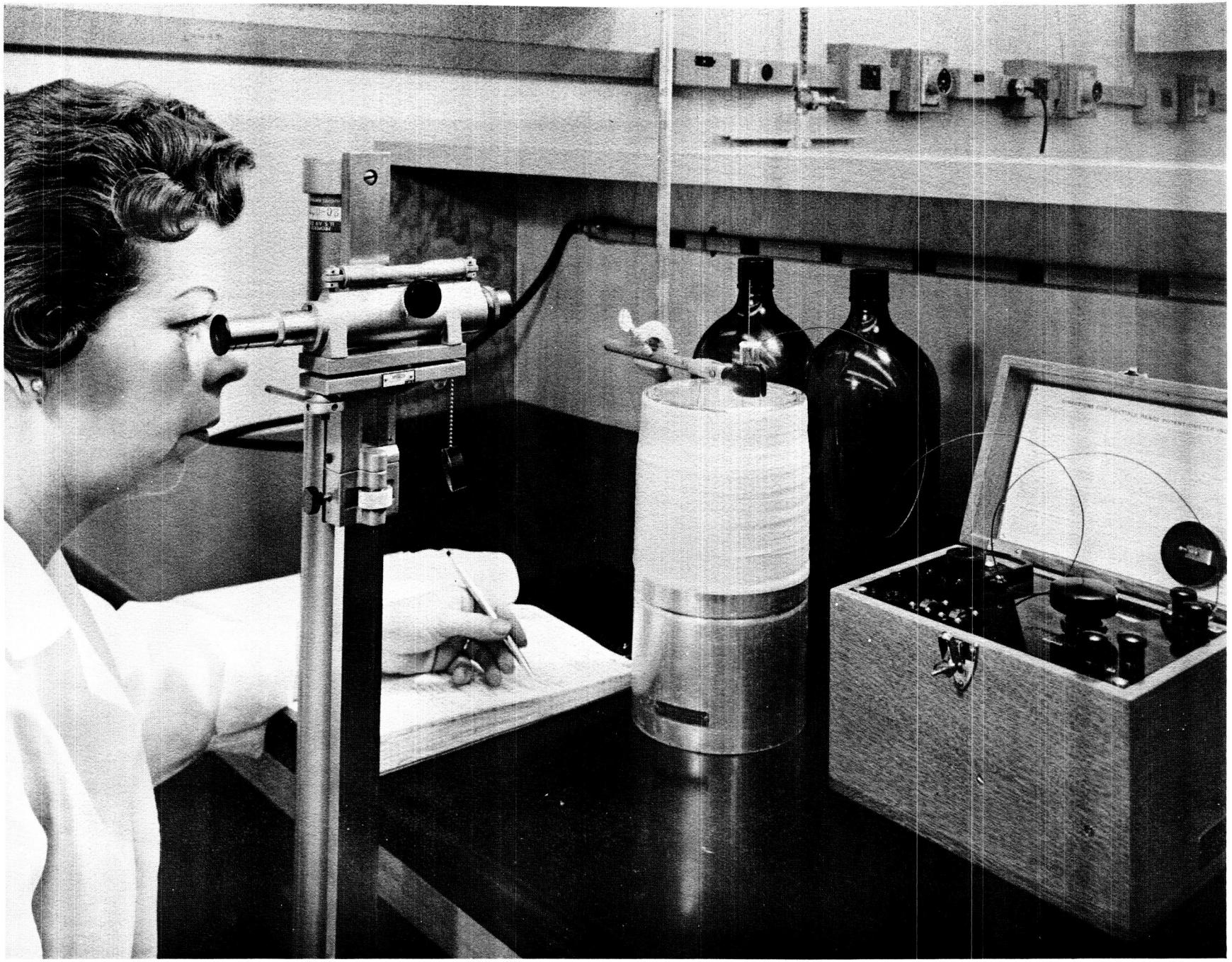


Figure IV-1. Thermal contraction apparatus.

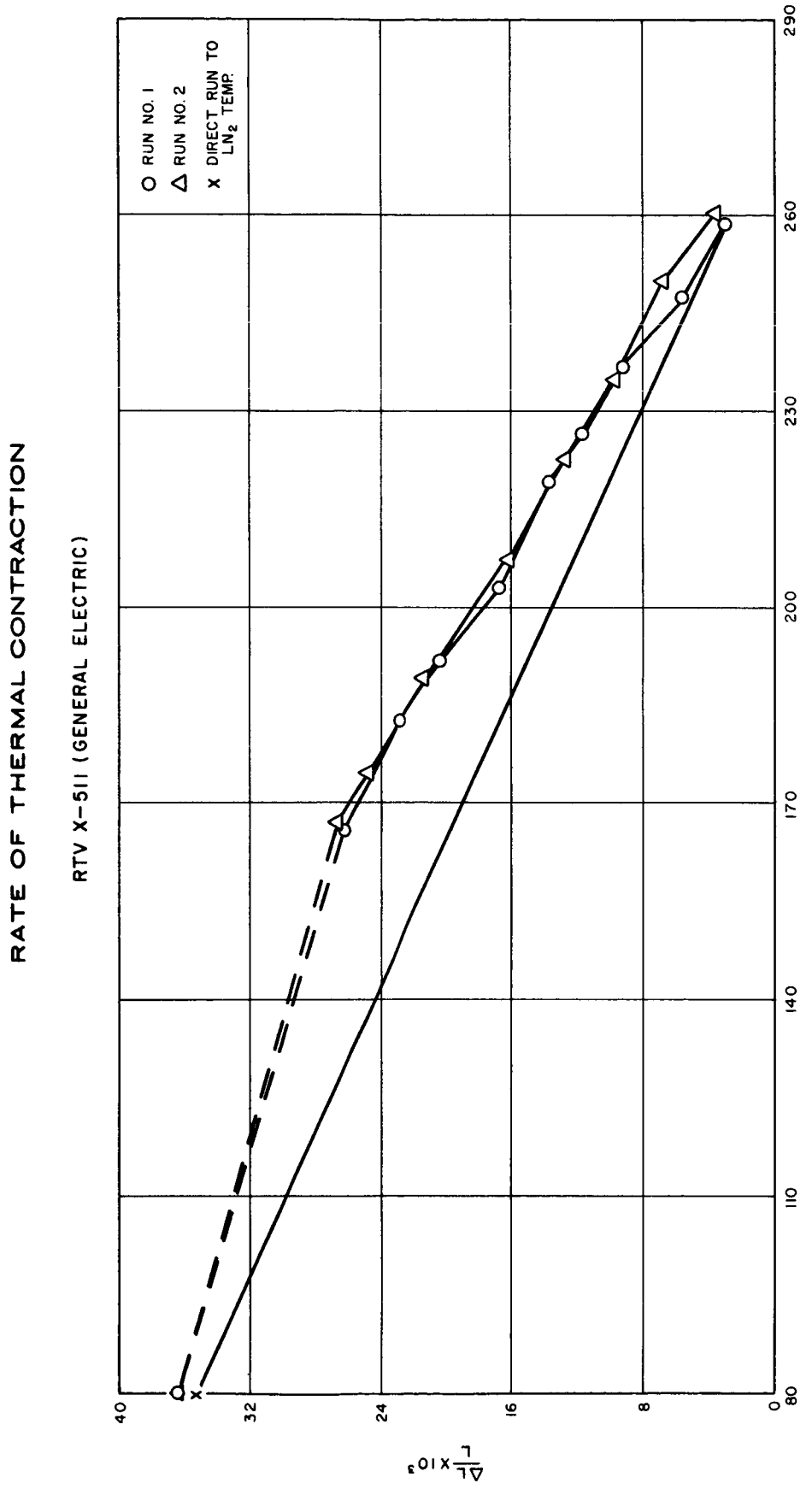


Figure IV-2. Rate of thermal contraction RTV X-511.

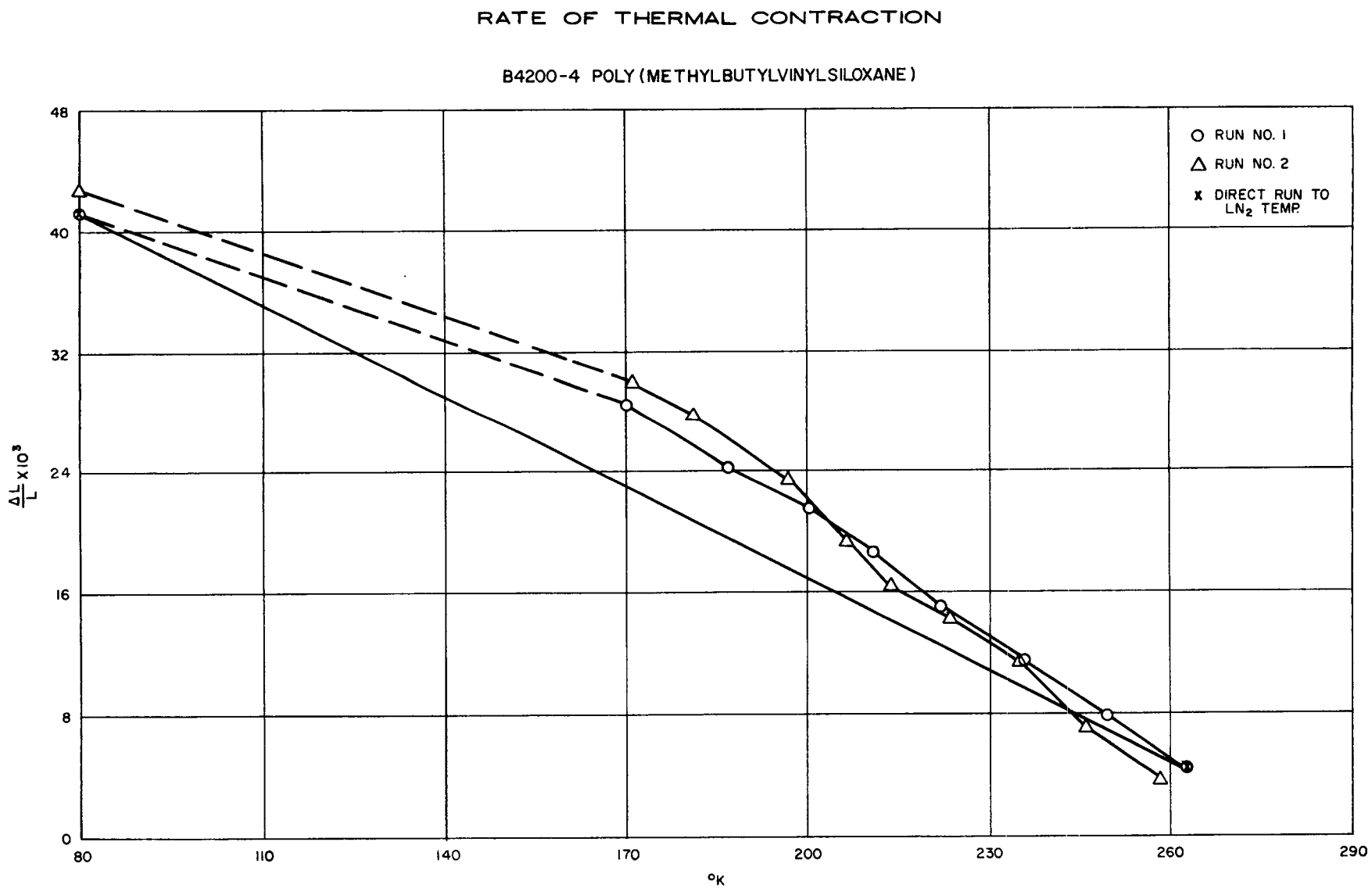


Figure IV-3. Rate of thermal contraction Poly(Methylbutylvinylsiloxane).

high, being 186 x 10^{-6} in/in/°C for the RTV-X511 and 215 x 10^{-6} in/in/°C for the poly (methylbutylvinylsiloxane). The overall coefficients for glass fabric reinforced systems based on these materials, however, will be much less, possibly approaching that of aluminum.

VIBRATION TESTING AT LIQUID NITROGEN TEMPERATURE

In use, the sealants will be exposed to shock and vibration loads of various frequencies and amplitudes. A test fixture was designed and a procedure was developed to determine if vibrations of various intensities, through a schedule of conditions specified by the contractor, would cause failure in a sealed joint. It was used here as an evaluation technique on candidate sealants found through previous screening tests to be the best available.

An RTV-X511 specimen, reinforced with four plies of 181 style glass fabric, was cured overnight and post-cured three days at 120°F. After curing, the specimen was vibration tested at 76°K. The candidate specimen withstood four of the five vibration loads to which it was subjected. The horizontal aluminum arm cracked at the bend radius during y-axis vibration tests in category 1. However, the sealed joint was still intact with the shorter specimen segment still attached to the plate. The metal fatigue failure must have occurred at or near the end of the last five minute run. Prior to this, the previous scanning traces made from the accelerometer input did not indicate any abnormalities.

The fixture consists of a hollow aluminum block with a removable plate forming one wall. The specimen was bonded to this wall with the sealant, and liquid nitrogen was poured into the hollow chamber to cool the entire fixture and specimen. The sealant thickness of the specimen was arbitrarily kept at a nominal 1/16-inch. A thermocouple was embedded in the sealant to measure the temperature and monitor the flow of liquid nitrogen. The thickness of the 1 x 6 inch aluminum segment of the specimen used in the tests was increased from 0.032 inch to 0.040 inch. The combined aluminum-RTV-X511 specimen had a 1/8-inch radius bend to give a free horizontal arm for loading to which an accelerometer was mechanically attached. The wall plate to which

the sealant was bonded was removable to allow new specimens to be inserted easily in the mounted fixture. The fixture assembly before and during testing are shown in Figure IV-4 and Figure IV-5 respectively.

The reinforced RTV-X511 sealant was subjected to the five vibration categories, at 76°K, specified by the sponsor, starting with the easiest category 5 and working backwards to the most severe category 1. The frequencies were scanned through the range of 20-2000 cps and resonance frequencies were held for either five or ten minute intervals. The results of the RTV-X511 specimen vibrated on the y-axis are summarized in Table IV-I.

Category	Resonance Frequencies	Loads at Resonance Frequencies ("G" Level)
5	59 cps (10 min.) 202 cps (10 min.)	1.7 5
4	49 cps (5 min.) 194 cps (5 min.)	3 10
3	52 cps (5 min.) 196 cps (5 min.)	5 15
2	55 cps (5 min.) 195 cps (5 min.)	5 50
1	51 cps (5 min.) 178 cps (5 min.)	10 40

Table IV-I

The reinforced Kel-F-800 specimen was prepared and vibration tested in the same manner as the RTV-X511 specimen. The Kel-F-800 specimen failed in the sealed joint during the y-axis vibration test. The failure of the specimen occurred at the end of category 3. Results of Kel-F-800 vibration test at 76°K are shown in Table IV-II.

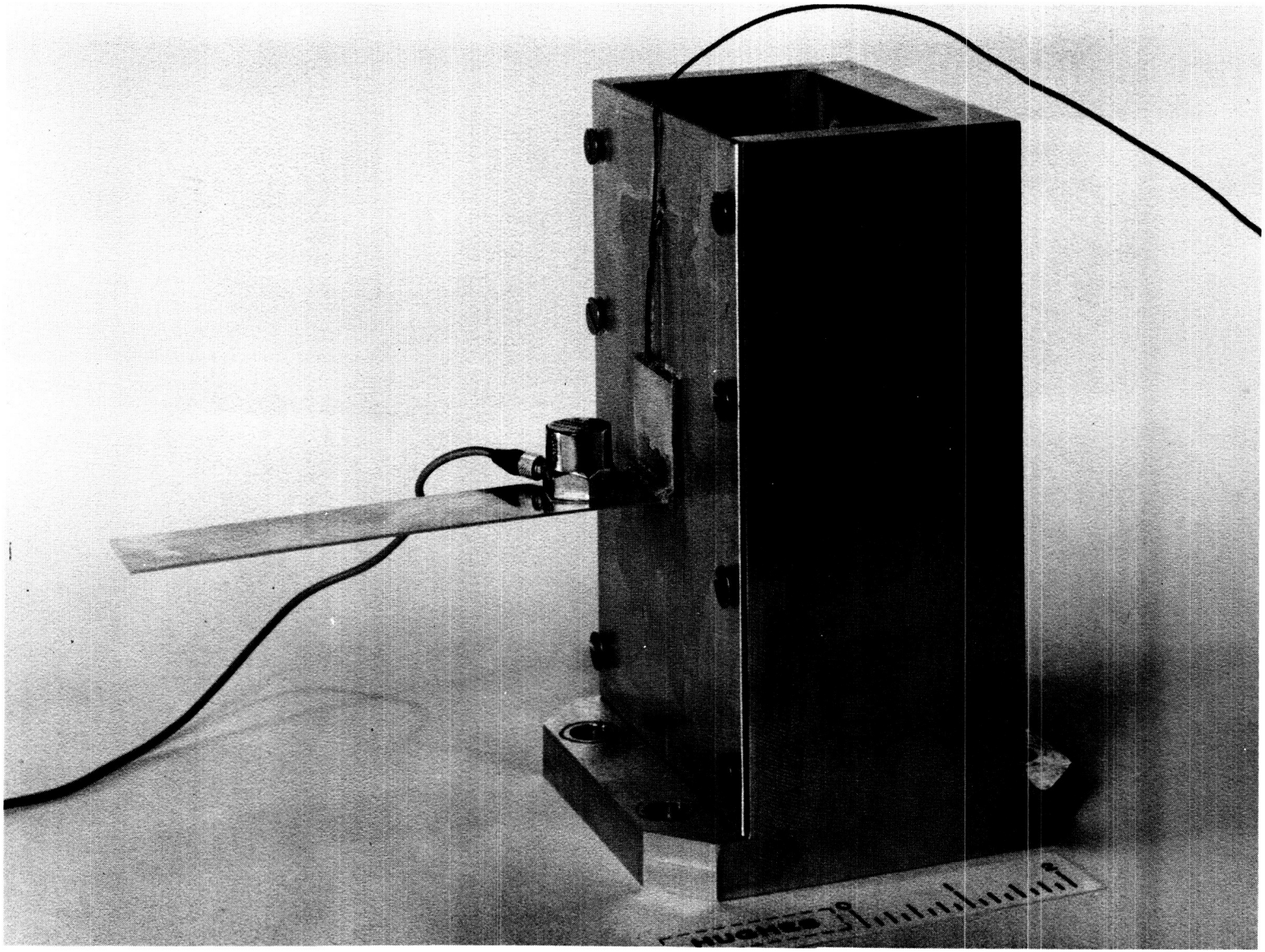


Figure IV-4. Vibration test fixture assembly - before testing.

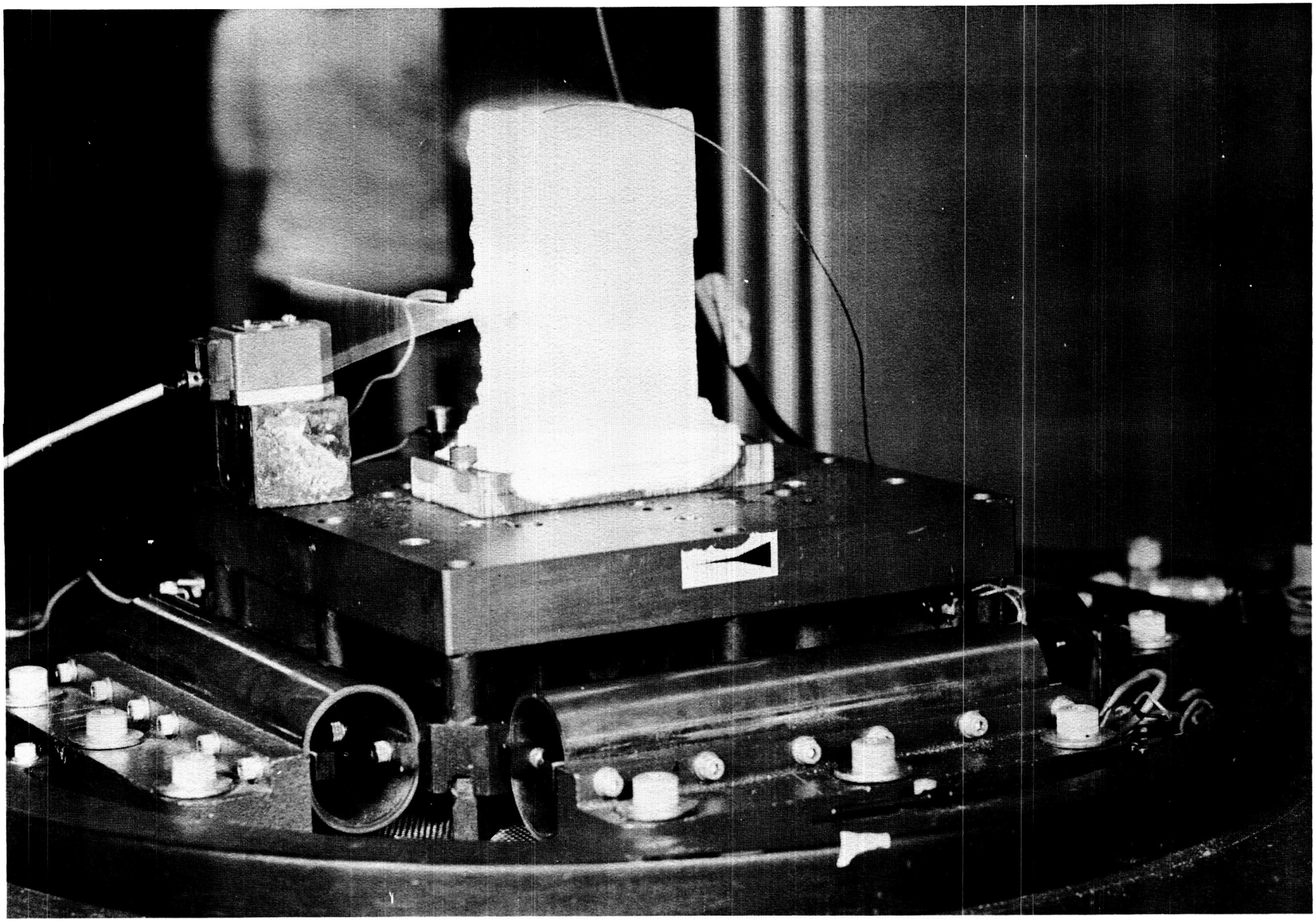


Figure IV-5. Vibration test fixture and specimen during test.

Category	Resonance Frequencies	Loads at Resonance Frequencies ("G" Level)
5	53 cps (10 min.)	1.4
	112 cps (10 min.)	5
4	50 cps (5 min.)	3
	132 cps (5 min.)	10
	168 cps (5 min.)	10

Table IV-II

Vibration tests of Adiprene L-100 cured with castor oil and reinforced with 181 style glass fabric were also carried out. Results were very encouraging, showing no failure throughout the schedule set forth by NASA.

SHOCK TESTING OF ADIPRENE-CASTOR OIL SEALANT

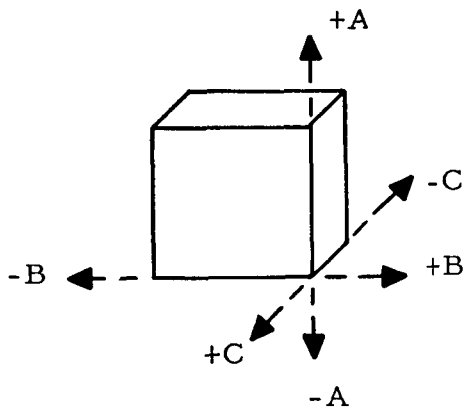
Following the successful vibration tests of Adiprene L-100, it was subjected to the shock tests specified by the contractor. The fixture developed for vibration testing was used in the shock test also. As in the vibration tests, the specimen was bonded to the wall with the sealant, and liquid nitrogen was poured into the hollow chamber to cool the entire fixture and specimen. The sealant thickness was arbitrarily kept at a nominal 1/16 inch. A thermocouple embedded in the sealant measured the temperature and monitored the flow of liquid nitrogen. The specimens used in the tests were 0.032 x 1 x 6 inch aluminum strips with a 1/8 inch radius bend to give a free horizontal arm for loading and to which an accelerometer was mechanically attached. The wall plate to which the sealant was bonded is removable to allow new speciments to be inserted easily in the mounted fixture.

The fixture and specimens were then subjected to a shock test in a tower that gives a triangular wave mode of shock. Six tests in each of three mutually perpendicular axes were performed without evidence of damage to the specimen. The results are given in Table IV-III and show that the Adiprene L-100-castor oil sealant reinforced with 181 style glass fabric resists severe shock, at 76°K.

Type Shock	No. of Shocks	Load (g)	Results
Triangular wave (saw-tooth)	6	20	No damage
Triangular wave (saw-tooth)	6	35	No damage
Triangular wave (saw-tooth)	6	65	No damage
Triangular wave (saw-tooth)	6	100	No damage

Table IV-III. Shock test - Adiprene L-100 cured with castor oil and reinforced with 181 style glass fabric.

These tests were repeated for each of the three mutually perpendicular axes as follows:



Order of Performance	
+A to -A	1
+B to -B	2
+C to -C	3

V. CRYOGENIC SEALANT FOR LOX TANK CREVICE

INTRODUCTION

An investigation has been carried out for a cryogenic sealant to protect the outer junction of the cylindrical and dome sections of liquid oxygen tanks against corrosion and particles. The protective surface coating of the two tank sections at this junction is omitted for welding purposes, and crevices are created in which foreign particles may become lodged. Problems of tank failure may be encountered when corrosion and large-particle embedment occur in the exposed crevices near the weld line. The aluminum walls of the tank junction have to be protected and the crevices filled by a sealant that can adhere down to the temperature of liquid oxygen while retaining sufficient flexibility or toughness to withstand the loads imposed by contractive movements during cool down. This sealant would not be in direct contact with the liquid oxygen at any time, although it would be cooled to LOX temperature.

In general, Adiprene L-100 cured with castor oil and filled with milled glass fibers passed thermal shock and tee-peel strength tests satisfactorily. Samples of the sealant and materials and process specifications (see Appendix) were sent to the Contractor. The sealant system was further improved by the addition of a catalyst which decreased the cure time at room temperature. Foamed-in-place versions of the formulation were investigated because of the considerable weight saving inherent in a foamed sealant. Sample kits of the improved sealant and of the most successful foamed sealant were also sent to the Contractor for evaluation, and appropriate revisions were made in the process specification. Study was made of the stability of the sealants after storage, and a modification of the improved sealant was formulated which permits reasonable storage in a premixed condition.

BASIC INVESTIGATION

For the basic investigation the physical characteristics of available sealants were studied to select the most suitable for application to the Dome LOX Tank (see section II), and Adiprene L-100 was judged most suitable. To determine if the base resin of this sealant would flow into the extremely small crevice near the dome tank weld, a tank section was fabricated to simulate the tank crevice. The crevice of the tank section was sealed (Figure V-1) with straight Adiprene L-100 (unfilled) in a way that could be done on a real tank. The surfaces were first degreased by flushing and draining with methyl ethyl ketone and primed with Chemlok 607 by filling and draining. After the primer had air dried, the sealant was poured to a depth of approximately six inches and cured at 80°C for four hours. (This cure can be accomplished at a lower temperature, supplied by heat lamps, over a longer period of time.) The flow was found to be fairly high, and the resin did fill areas in which the gap was estimated to be about 0.005 inch. A resonance bond tester manufactured by the Fokker Aircraft Company was used with a No. 3814 transducer to check for void areas. Several small areas were found, indicating areas of poor adhesion or trapped air.

GLASS-FILLED SEALANT

Other simulated tank sections were fabricated and sealed to approximately five inches with a sealant consisting of Adiprene L-100 cured with castor oil and filled with 1/4 inch milled glass fibers. The metal surfaces of these sections were also cleaned by flushing and draining with methyl ethyl ketone and primed with Chemlok 607 by filling and draining. After being cured for four hours at 80°C, the tank sections were subjected to thermal shock by repeating immersion in liquid nitrogen. They passed this test without evidence of failure. The peel strength of the sections was then tested at room temperature and at 76°K; results are given in Table V-I.

Because of the encouraging results of these tests, tee-peel strength tests at room temperature and 76°K were performed.

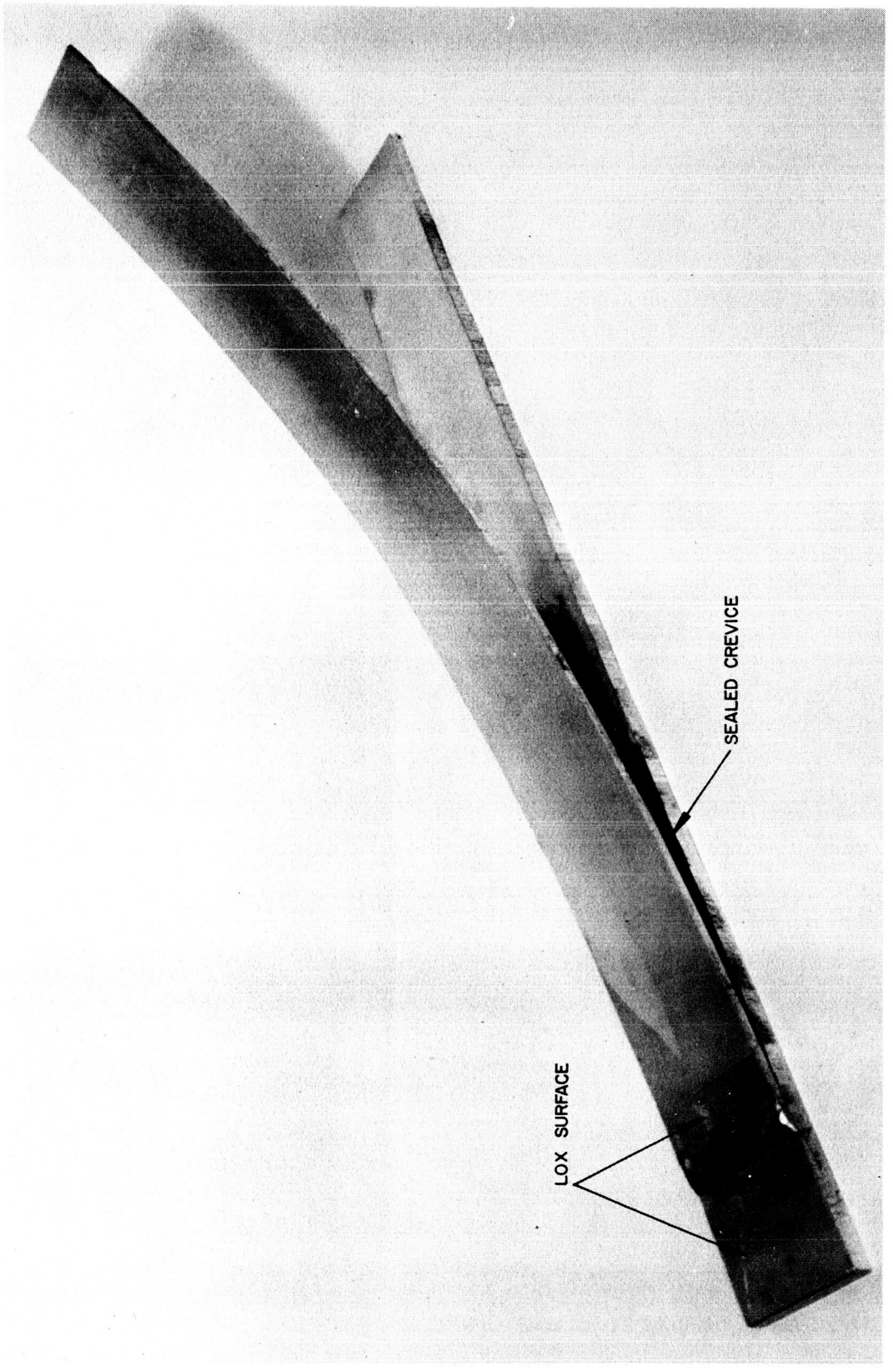


Figure V-1. Sealed simulated LOX tank section.

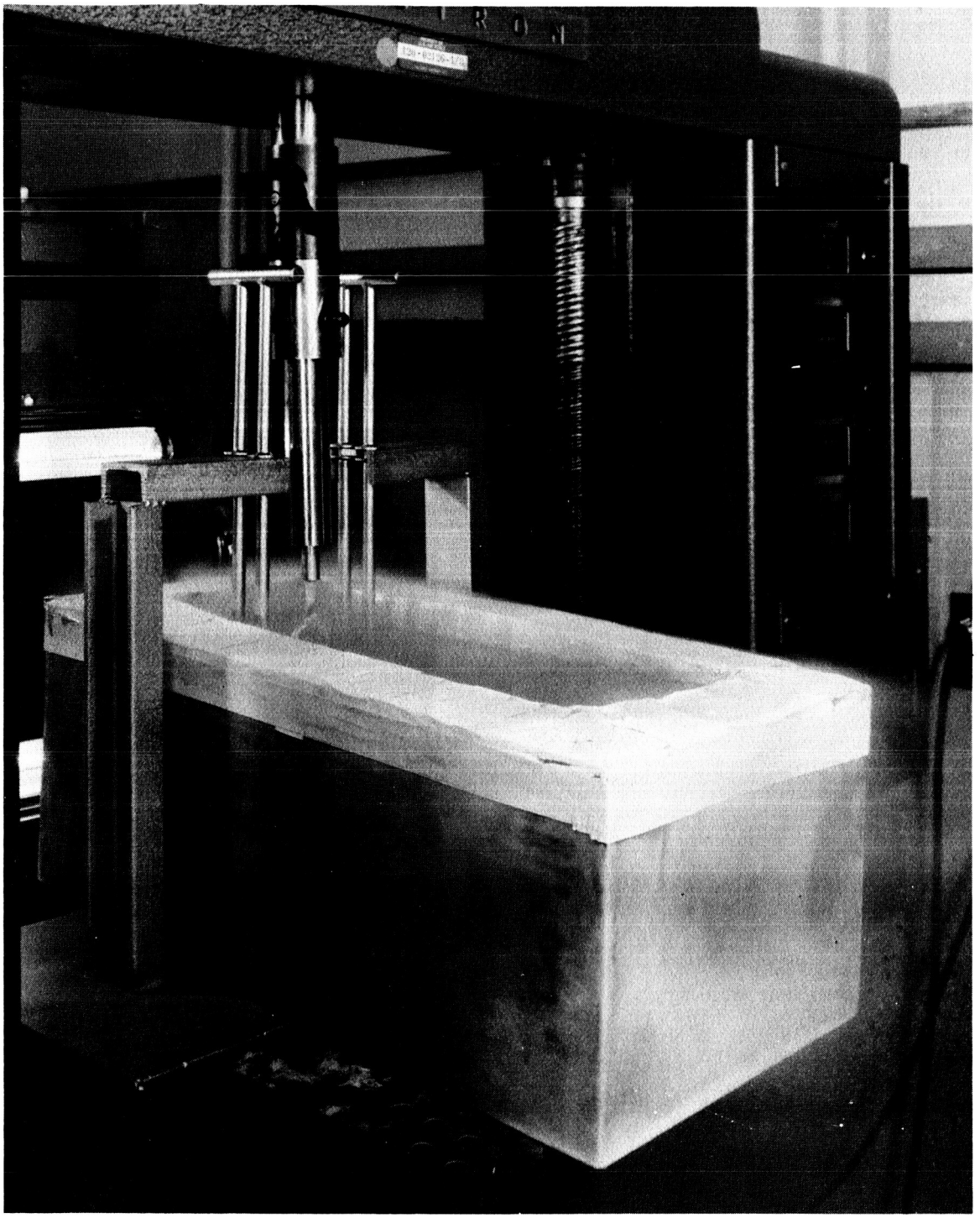


Figure V-2. Peel test apparatus.

Test Temperature	Peel Strength (pounds)			Type of Failure
	Initial	High	Low	
Room temperature	138	130	103	Cohesive
Room temperature	166	137	87	Cohesive
76°K	86	66.5	23.5	Approx. 90 percent adhesive
76°K	92	60.5	18.2	Approx. 90 percent adhesive

Table V-I. Peel strength of simulated LOX tank sections.

Specimens were prepared consisting of 0.020 x 1 x 10-inch strips of 7075-T6 aluminum, bonded together with sealant approximately 1/16 inch thick. Testing was done on an Instron tensile testing machine that provided a peel speed of 12 inches per minute. The test apparatus is shown in Figure V-2. The data given in Table V-II represent the initial breaking strength to start peeling and the high and low values recorded during the peeling "steady state".

Test Temperature	Tee-Peel Strength (pounds/inches)		
	Initial	High	Low
Room temperature	8.0	8.0	4.0
Room temperature	7.0	8.0	7.0
Room temperature	12.2	off scale	6.2
Room temperature	24.4	25.0	13.7
Room temperature	12.3	20.3	11.0
76°K	5.3	12.4	1.5
76°K	3.7	11.8	1.6
76°K	4.6	11.9	4.?
76°K	2.5	13.4	2.5
76°K	4.2	11.0	1.7

Table V-II. Tee-Peel strength of candidate LOX Tank crevice sealant.

Curing Process Study

A study of cure time and temperature was made to determine the conditions necessary for the use of Adiprene-glass fiber LOX tank sealants. The results indicated the need for a heat source, such as infrared lamps, to cure the sealant in a reasonably fast time. In 20-gram batches curing was accomplished in 45 hours at room temperature. At 100° F it took 37 hours. Cures were timed at progressively higher temperatures with the result that a reasonably cured sealant may be obtained in approximately six hours at a temperature obtainable in the field with auxiliary heating equipment. It was recognized, however, that curing the sealant at ambient temperatures would be more advantageous.

A materials specification (HMS 16-1351) and a corresponding process specifcation (HP 5-14) for the glass fiber-filled Adiprene L-100 plus castor oil system for the LOX tank crevice sealant were written. Both specifications are included in the Appendix.

In an attempt to make possible curing of the sealant at room temperature, studies were made of the effects of T-9, a stannous octoate catalyst, manufactured by the Metal and Thermit Corporation. From one to five drops of catalyst T-9 were added to resin samples consisting of 12.5 grams of Adiprene L-100 and 4.5 grams of castor oil. Each sample was allowed to cure at room temperature for six hours and 18 hours. A full cure at room temperature was obtained after 18 hours with the samples to which five drops of T-9 catalyst had been added. This cure time can be compared with the 45 hours at room temperature required for the cure of the resin system without a catalyst. Results for all the samples are summarized in Table V-III.

Crevice Foamed Sealant

Because a considerable saving in weight could be realized from the use of a foamed-in-place crevice sealant, work was begun on the development of such a foam material. Five formulations (Table V-IV) were tried. These were similar to those previously developed so that the foam sealants would have comparable thermal contraction and peel

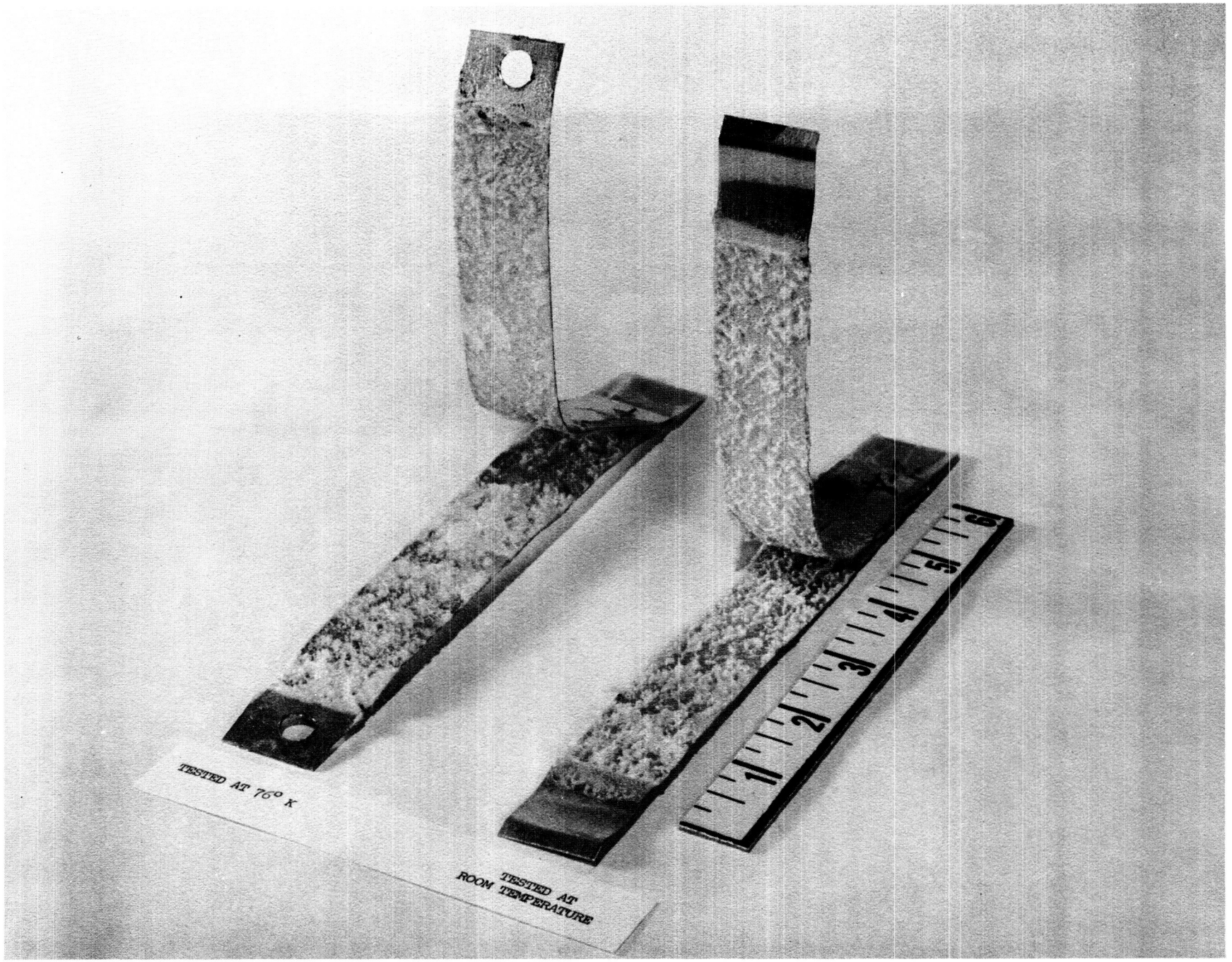


Figure V-3. Peel test specimens of LOX tank crevice sealant.

T-9 Added (drops)	Time of Cure (hours)	Condition
1	6	Flows
2	6	Flows
3	6	Little Flow -- tacky
4	6	Very Little Flow -- tacky
5	6	No Flow -- tacky
1	18	Very Little Flow -- tacky
2	18	No Flow -- tacky
3	18	No Flow -- slightly tacky
4	18	No Flow -- soft but considered cured
5	18	Cured -- no flow and not tacky

Table V-III. Effect of T-9 catalyst on resin cure.

strength properties. Formulation No. (FN) 5 gave the most satisfactory foam: it has a usable pot life and cures in 24 hours at room temperature. A simulated tank section was filled to a foamed depth of five inches and immersed repeatedly in liquid nitrogen without evidence of failure in the section.

Tee-peel specimens were then prepared with the foamed formulation No. 5 Aluminum strips, 0.020 x 1 x 2 inches, were etched by immersion in a mixture of 30 parts of H_2O by weight, four parts concentrated H_2SO_4 by weight, and one part $Na_2Cr_2O_7$ by weight. After being etched in this solution for ten minutes at 140-160°F, the strips were rinsed in distilled water and air dried. They were primed with Chemlok 607 and allowed to air dry one hour. After drying, the strips were bonded together with a nominal 1/16-inch thickness of the foamed sealant and cured for 24 hours at room temperature before testing. Peel test results are given in Table V-V and representative specimens after test are shown in Figure V-3.

Revision A to HP 5-14 was prepared and sent to the Contractor together with preweighed sample kits of the foam sealant for practical evaluation. This revision is included in the Appendix.

FN*	Material	Amount (grams)	Results
1	Adiprene L-100 MOCA[1] XF-1034[2] Dabco[3] Water Milled glass fibers	100 9.7 2 0.2 0.2 31.6	Foamed to approximately 3 times original volume Very short pot life Foam lacks flexibility
2	Adiprene L-100 Castor Oil XF-1034 Triethylamine Water Fiberfrax fibers[4]	100 36 8 8.4 8.4 40.4	Foamed to approximately 3 times original volume Poor texture Short pot life Flexible
3	Adiprene L-100 Castor Oil XF-1034 Triethylamine Water Fiberfrax fibers	100 36 2 1.6 1.6	Foamed to approximately 3 times original volume Poor texture 30 to 45 minute pot life Flexible
4	Adiprene L-100 Caster Oil XF-1034 Benzyldimethylamine Water Fiberfrax fibers	100 24.8 2 0.8 0.8 36.4	Foamed to approximately 3 times original volume Poor texture 30 to 45 minute pot life
5	Adiprene L-100 Caster Oil XF-1034 Benzyldimethylamine Water Fiberfrax fibers	100 24.8 2 0.4 0.8 42.6	Foamed to approximately 3 times original volume Good texture 30 to 45 minute pot life Flexible

*FN = formulation number

[1]MOCA = 4,4'-methylene-bis-(2-chloroaniline) (du Pont)

[2]XF-1034 = silicone oil surfactant (General Electric)

[3]Dabco = triethylenediamine (Houdry Process Corp.)

[4]Fiberfrax = short strand refractory fiber (Carborundum Co.)

Table V-IV. Formulations of crevice foamed sealant.

Specimen No.	Peel Strength (pounds/inch)			Failure (percentage)		Test Temperature
	Initial	High	Low	Adhesive	Cohesive	
1	31.7	31.7	7.0	90	10	Room
2	24.2	25.7	4.3	95	5	Room
3	30.3	30.3	6.5	85	15	Room
4	36.3	36.3	27.5	20	80	Room
5	40.0	41.3	29.5	30	70	Room
6	10.5	10.5	0.2	95	5	76° K
7	10.8	10.8	0.7	98	2	76° K
8	11.1	11.1	0.0	99	1	76° K
9	3.9	3.9	0.5	95	5	76° K
10	*	4.2	0.0	85	15	76° K
11	5.4	5.4	0.6	50	50	76° K

*Initial break occurred during adjustment of specimen in test grips.

Table V-V. Tee-Peel tests of improved foamed crevice sealant.

Use of Catalyst with Foamed Sealant

Since the addition of catalyst T-9 to the original formulation had materially shortened the cure time, studies were made to ascertain if a similar effect could be obtained by the addition of a catalyst to the foamed resin system. Attention was focused especially on the production of a lower density foam and on better foam cell structure, in addition to the desired shorter curing time. In the improvement studies of the foam sealant, HP 5-14 Revision A, was used as the control; variations from the control formulation and processing included reduced ratios of T-9 catalyst, increased ratios of T-9 catalyst, reduced water, increased water, and omitted water (due to a small amount of water in the castor oil). Since the desired improvements in the foamed sealant could conceivably be accomplished by the use of new materials and techniques, several new materials were included in the evaluations: (1) General Electric's SF-1066 surfactant, an improved and more hydrolytically

stable version of SF 1034; (2) Witco's Fomrez C-2, a stannous catalyst that has been used successfully in many "one shot" polyether foam formulations; and (3) benzyldimethylamine catalyst. The experimental formulations are listed in Table V-VI. These various formulations were tested for foam characteristics at ambient, 100° F, 110° F, and 120° F temperatures for a period of approximately 8 hours.

Adjustment of the variables indicated that a significant difference in foam quality resulted from an increase in the amount of T-9 catalyst. The foam was definitely inferior to the control because of the more rapid resin polymerization that limited the foaming action. Adjustments were then made by variations in the combinations of these variables. It was found in Formulation No. (FN) 7 that, when both the T-9 catalyst and water were increased, a faster cure resulted; the water provided a CO_2 formation of sufficient quality and rapidity to give a good foam. At ambient, 110° F, and 120° F cure temperatures, foams of three times the original volume resulted with good cell structure and elastic recovery. However, with the exception of FN's 7, 8, 13, and 14, none of the experimental formulations produced foam characteristics that were desirable for crevice sealing applications. The four excepted formulations were progressively better, producing satisfactory characteristics at all four curing temperatures. FN's 1, 10, 7, and 8 are similar to each other with the exception of the substituted SF 1066 surfactant.

The General Electric SF 1066 surfactant was substituted in identical ratios into the control formulation to determine the effect of the new surfactant. Observations and results indicated no adverse effect nor any improvement of the control formula when mixed as described in HP 5-14, Revision A.

Effect of Storage on Sealant Components

Communication from the contractor stated that the original foam sealant submitted for evaluation had failed to foam adequately when it was mixed according to HP 5-14, Revision A. An investigation was made to determine the cause of this failure. Results indicated that the

FN*	Material	Amount	FN*	Material	Amount
1	Adiprene L-100 Resin	50.0 grams	8	Adiprene L-100 Resin	50.0 grams
	Fiberfrax (washed) Fibers	21.3 grams		Fiberfrax (washed) Fibers	21.3 grams
	Castor Oil, USP	12.4 grams		Castor Oil, USP	12.4 grams
	SF 1034	1.0 gram		SF 1066	1.0 gram
	T-9 Catalyst	20 drops		T-9 Catalyst	25 drops
	Water (distilled)	4 drops		Water (distilled)	8 drops
2	Adiprene L-100 Resin	50.0 grams	9	Adiprene L-100 Resin	50.0 grams
	Fiberfrax (washed) Fibers	21.3 grams		Fiberfrax (washed) Fibers	21.3 grams
	Castor Oil, USP	12.4 grams		Castor Oil, USP	12.4 grams
	SF 1034	1.0 gram		SF 1066	1.0 gram
	T-9 Catalyst	15 drops		T-9 Catalyst	25 drops
	Water (distilled)	4 drops		Water (distilled)	1 drop
3	Adiprene L-100 Resin	50.0 grams	10	Adiprene L-100 Resin	50.0 grams
	Fiberfrax (washed) Fibers	21.3 grams		Fiberfrax (washed) Fibers	21.3 grams
	Castor Oil, USP	12.4 grams		Castor Oil, USP	12.4 grams
	SF 1034	1.0 gram		SF 1066	1.0 gram
	T-9 Catalyst	25 drops		T-9 Catalyst	20 drops
	Water (distilled)	4 drops		Water (distilled)	4 drops
4	Adiprene L-100 Resin	50.0 grams	11	Adiprene L-100 Resin	50.0 grams
	Fiberfrax (washed) Fibers	21.3 grams		Fiberfrax (washed) Fibers	21.3 grams
	Castor Oil, USP	12.4 grams		Castor Oil, USP	12.4 grams
	SF 1034	1.0 gram		SF 1066	1.0 gram
	T-9 Catalyst	20 drops		T-9 Catalyst	25 drops
	Water (distilled)	2 drops		Water (distilled)	3 drops
5	Adiprene L-100 Resin	50.0 grams	12	Adiprene L-100 Resin	50.0 grams
	Fiberfrax (washed) Fibers	21.3 grams		Fiberfrax (washed) Fibers	21.3 grams
	Castor Oil, USP	12.4 grams		Castor Oil, USP	12.4 grams
	SF 1034	1.0 gram		SF 1066	1.0 gram
	T-9 Catalyst	20 drops		T-9 Catalyst	32 drops
	Water (distilled)	Omitted		Water (distilled)	4 drops
6	Adiprene L-100 Resin	50.0 grams	13	Adiprene L-100 Resin	50.0 grams
	Fiberfrax (washed) Fibers	21.3 grams		Fiberfrax (washed) Fibers	21.3 grams
	Castor Oil, USP	12.4 grams		Castor Oil, USP	12.4 grams
	SF 1034	1.0 gram		SF 1066	1.0 gram
	T-9 Catalyst	20 drops		Benzyldimethylamine Catalyst	20 drops
	Water (distilled)	8 drops		Water (distilled)	4 drops
7	Adiprene L-100 Resin	50.0 grams	14	Adiprene L-100 Resin	50.0 grams
	Fiberfrax (washed) Fibers	21.3 grams		Fiberfrax (washed) Fibers	21.3 grams
	Castor Oil, USP	12.4 grams		Castor Oil, USP	12.4 grams
	SF 1034	1.0 gram		SF 1066 Surfactant	1.0 gram
	T-9 Catalyst	25 drops		Formez C-2 Catalyst	32 drops
	Water (distilled)	8 drops		Water (distilled)	4 drops

*FN = Formulation Number

Table V-VI. Experimental formulations using catalysts with foamed sealant.

pre-mixed component B, listed in HP 5-14, Revision A, had become unstable after prolonged storage and that the SF 1034 surfactant had hydrolyzed in the container. SF 1034 is a copolymer of a polydimethylsiloxane and a polyoxyalkylene fluid and is susceptible to hydrolysis across the Si-O-C bond. In the presence of moisture, hydrolysis is catalyzed by an acid. The ether linkages in the polyoxalkylene fluid will form peroxides by reaction with dissolved oxygen or with oxygen from the air. These unstable peroxides then readily react with the OH groups present in the polyoxyalkylene fluid and also with moisture to form a weak acid or aldehyde. In addition, the possibility existed that the T-9 catalyst in the original foam sealant formulation reacted with the silicone-based surfactant (SF 1034). This reaction might make it necessary to supply the final formulation in three separate components.

Samples of surfactants were evaluated to determine the hydrolytic stability in foamed sealant formulations, and it was found that the General Electric SF 1066 surfactant will satisfy the stability requirement. Storage stability evaluations were then made with the pre-mixed component B; with both the SF 1034 and SF 1066 surfactants; and with Fomrez C-2, T-9, and benzyldimethylamine catalysts. Formulations utilizing these components in different combinations were studied after 2, 10, 20, and 30 days. Storage for only two days of component B containing the T-9 catalyst resulted in an inferior foam with decreased volume. It was found, however, that if the T-9 were added to component B (which had been stored for 10 days) immediately before the mixing of components A and B, a satisfactory foam resulted. Storage of a complete, pre-mixed, two-component system is not recommended. The sealant should either be mixed according to HP 5-14, Revision A, immediately before the LOX tank crevices are sealed or supplied as a three-component system. When storage of complete pre-mixed components is mandatory, studies show that the benzyldimethylamine catalyst can be substituted for T-9 catalyst. As a result of the storage studies, it is conditionally possible to supply two-component systems with benzyldimethylamine as a catalyst and SF 1066 as a surfactant.

The studies indicated that these materials apparently do not interact for 32 days at room temperature. For longer storage, materials pre-weighed and pre-packaged would require separate and individual containers. The foam failures after storage of pre-mixed component B using SF 1034, SF 1066, Fomrez C-2, and T-9 were probably due to the incompatibility of these materials in the presence of water and with subsequent decreased catalytic activity of component B. Storage stability samples and results are shown in Table V-VII.

At the request of the contractor, new LOX tank crevice sealant formulations, packaged individually, were submitted for re-evaluation (Table V-VIII). Kit A represents the original formulation described in HP 5-14 and Kit B, the newer foam formulation of HP 5-14, Revision A.

It is concluded from these studies that, when benzyldimethylamine and SF 1066 are substituted as the catalyst and surfactant, respectively, in component B of the sealant system, they produce a foam that is significantly better than the foams made with the T-9 or Fomrez C-2 catalysts and SF 1034 surfactant. Both T-9 and Fomrez C-2, combined with SF 1066, did produce foams that were satisfactory when mixed immediately with component A. However, these catalysts, after storage, become instable in component B because of the presence of the distilled water in this component. Water decreases the catalytic activity of the foam after storage.

Studies also showed that the benzyldimethylamine catalyst and the SF 1066 surfactant in component B may be satisfactory for storage. Apparently these materials do not interact for periods up to 32 days. It was concluded that benzyldimethylamine and SF 1066 should be substituted for T-9 and SF 1034. These substitutions are reflected in specification HP 5-14, Revision B which is included in the Appendix.

Revision B, HP 5-14, also corrects a mixing error that appears in Revision A. Specification HP 5-14, Revision A, states in paragraph 3.3.2.3 "that each component may be heated to 150° F individually to facilitate mixing". This statement is valid only for HP 5-14, not for either Revision A or B.

FN*	Material	Amount	Storage Time (days)	Observation of Component B During Storage	Storage Remarks
1	Adiprene L-100 Fiberfrax (washed) fibers Castor Oil, USP SF 1034 T-9 Catalyst Water (distilled)	50.0 grams 21.3 grams 12.4 grams 1.0 gram 20 drops 4 drops	2 10	Clear after mixing Partially cloudy after 2 days of storage. Semi-gelled. Storage discontinued	See below**
2	Adiprene L-100 Fiberfrax (washed) fibers Castor Oil, USP SF 1066 T-9 Catalyst Water (distilled)	50.0 grams 21.3 grams 12.4 grams 1.0 gram 20 drops 4 drops	2 10 20	Clear after mixing Completely cloudy after 2 days Semi-gelled Storage discontinued	See below**
3	Adiprene L-100 Fiberfrax (washed) fibers Castor Oil, USP SF 1066 Water distilled T-9 Catalyst added the day of mixing with Comp. "A"	50.0 grams 21.3 grams 12.4 grams 1.0 gram 4 drops 20 drops	2 10 20 34	Cloudy after mixing Cleared up and remained clear during the entire storage	See below**
4	Adiprene L-100 Fiberfrax (washed) fibers Castor Oil, USP SF 1034 Water (distilled) T-9 Catalyst added the day of mixing with Comp. "A"	50.0 grams 21.3 grams 12.4 grams 1.0 gram 4 drops 20 drops	2 10	Turned hazy after mixing Completely cloudy the third day	Two days - Increased 3 times in volume during the first 5 hours at room temperature. Cured overnight. Cured sample increased to 3-1/2 times in volume. Good elastic recovery. Ten days - Increased 3 times in volume at room temperature. Cured overnight. Good elastic recovery.
5	Adiprene L-100 Fiberfrax (washed) fibers Castor Oil, USP SF 1066 Benzyldimethylamine Catalyst Water (distilled)	50.0 grams 21.3 grams 12.4 grams 1.0 gram 20 drops 4 drops	2 8 16 32	Slightly hazy after mixing Cloudy after 2 days Remained cloudy during the entire storage	Two days - Cured overnight at room temperature, increased 3-1/2 times original volume. Good elastic recovery. Eight days - Increased 3-1/2 times in volume, room temperature. Cured overnight. Good elastic recovery. Sixteen days - Increased 3 times in volume within first 7 hours. Cured overnight at room temperature. Good elastic recovery. Thirty-two days - Cured overnight. Sample increased 3 times in volume. Good elastic recovery.
6	Adiprene L-100 Fiberfrax (washed) fibers Castor Oil, USP SF 1066 Fomrez C-2 Catalyst Water (distilled)	50.0 grams 21.3 grams 12.4 grams 1.0 gram 32 drops 4 drops	2	Clear to hazy	Two days - Sample increased 4 times in volume during the first 1-1/2 hours. Cured overnight at room temperature. Tack free after 6 hours. Good elastic recovery.
7	Adiprene L-100 Fiberfrax (washed) fibers Castor Oil, USP SF 1066 Fomrez C-2 Catalyst Water (distilled)	50.0 grams 21.3 grams 12.4 grams 1.0 gram 20 drops 4 drops	2	Clear to hazy	Two days - Sample increased once in volume. Cured overnight at room temperature. Poor elastic recovery.

*FN = Formulation Number

**Storage Remarks

Two days - Foam increased 2-1/2 times original volume during the first 5 hours at room temperature. Cured overnight. Sample increased to 3 times original volume. Good elastic recovery.

Ten days - Increased 3 times in volume. Cured overnight at room temperature. Good elastic recovery.

Twenty days - Cured overnight at room temperature. Sample increased 3 times in volume after 7 hours.

Thirty-four days - Cured overnight at room temperature. Sample increased 3 times in volume. Fair elastic recovery.

Table V-VII. Storage evaluation of pre-mixed Component B

Function	Code No.	Material	Amount (grams)	Quantity Submitted (grams)
KIT A (original formulation, HP 5-14)				
Resin	A-1	Adiprene L-100	100.0	454.0
Filler	A-2	Milled Glass Fibers	50.0	228.0
Curing Agent	A-3	Castor Oil	36.0	163.0
Primer	A-4	Chemlok 607	--	--
KIT B (new foam formulation HP 5-14, Revision A)				
Resin	B-1	Adiprene L-100	100.0	454.0
Filler	B-2	Fiberfrax (Refractory Fibers)	42.6	194.0
Curing Agent	B-3	Castor Oil	24.8	112.0
Surfactant	B-4	SF 1034	2.0	9.0
Catalyst	B-5	Stannous Octonoate (T-9)	1.0	4.5
Blowing Agent (Not submitted)	B-6	Distilled Water	0.4	1.8
Primer	B-7	Chemlok 607	--	--

Table V-VIII. Formulations resubmitted to contractor.

VI. CONCLUSIONS AND FUTURE WORK

Of the available LOX compatible polymers for sealant bases, only Kel-F 800 was found to have promise. When suitably primed and reinforced, its adhesion and flexibility at 76°K made it the best candidate for use in contact with LOX. Difficulty in the removal of solvents necessary for its processing, however, results in a LOX impact resistance level too low for acceptance by the Contracting Agency.

The glass fabric reinforced Adiprene L-100 polyurethane prepolymer cured with castor oil and the reinforced RTV-X511 remain as the best cryogenic sealants for use in non-LOX applications.

Some success has been accomplished in the synthesis of new modified silicone polymers. Further work will be devoted mainly to the continuation of the synthesis program involving not only silicone polymers but new polyurethane materials and others agreed upon by the contractor's technical representative. The work will include testing and evaluation at 20°K. It will be a basic study with complete polymer characterization. From this work, the most promising candidates will be used for the compounding of sealants.

A series of compounding studies and evaluations have resulted in a LOX tank dome sealant evolved from the basic Adiprene L-100, castor oil system, and this sealant is described in HP 5-14, Revision B, which is included in the Appendix.

APPENDICES

HUGHES PROCESS AND MATERIAL SPECIFICATIONS

"A"

HP 5-14

SEALING, GLASS FIBER FILLED POLYURETHANE COMPOUND, FOR LOX TANK APPLICATION

CODE INDENT. NO. 82577

ELECTRONIC MFG. DIV. / MISSILE MFG. DIV.	HUGHES AIRCRAFT COMPANY CULVER CITY, CALIFORNIA HUGHES PROCESS	HP 5-114	REV. LTR.
		PAGE 1 OF 4	
MATLS. TECHNOLOGY DEPT. S.W. Lemer/L.C. Palmer	SEALING, GLASS FIBER FILLED POLYURETHANE COMPOUND, FOR LOX TANK APPLICATION	ISSUE DATE 18 March 63	REVISION DATE
		PREPARED BY L.C. Palmer	

FOR ENGINEERING USE ONLY

1. SCOPE

1.1 Scope.- This specification covers the sealing and filling of areas between liquid oxygen tank domes and outer walls of launch vehicles. Sealing material used is a glass fiber filled polyurethane.

NOTE: THIS MATERIAL SHALL NOT BE USED WHERE IT WILL BE DIRECTLY EXPOSED TO LIQUID OXYGEN (SEE 5.2).

2. APPLICABLE DOCUMENTS

2.1 The following document forms a part of this specification to the extent specified herein:

SPECIFICATIONS

Hughes Aircraft Company

HMS 16-1351 Plastic Resin, Polyurethane Elastomer, For Cold Temperature Sealant

3. REQUIREMENTS

3.1 Finished Product.-

3.1.1 Workmanship.- The sealant shall be a fully cured elastomer, light grey in color, having no areas of softness as evidence of improper or incomplete mixing. Unless otherwise specified by the engineering drawing, crevices shall be uniformily filled to a depth of approximately 4 inches. Inspection shall be as specified in 4.1.

3.1.2 Peel Strength.- Cured sealant shall have the following peel strength when tested as specified in 4.2.2:

Temperature	Peel strength, pounds per inch
Room	4.0
-320°F	1.5

3.1.3 Thermal Shock.- Cured sealant shall show no visible signs of delamination when subjected to the thermal shock test specified in 4.2.3.

3.2 Materials.- The sealant, curing agent, and primer required by this process shall be in accordance with Table I.

TABLE I -- MATERIALS

Material	Designation	Applicable Specification
Resin	Adeprene L-100	HMS 16-1351
Filler	Milled Glass Fibers[1]	-
Curing Agent	Castor Oil, USP	-
Primer	Chemlok 607[2]	-

1/ Milled glass fibers shall be 1/32 to 1/4 inch long and may be obtained from Owens Corning Fiberglas, 5933 Telegraph Road, Los Angeles 22, California.

2/ May be obtained from the Hugheson Chemical Co., Erie, Pennsylvania.

3.3 Procedure.-

3.3.1 Surface Treatments.-

3.3.1.1 Cleaning.- Aluminum tank walls shall be thoroughly cleaned with acetone or methyl ethyl ketone. Cleaning shall be accomplished by wiping the aluminum with clean cloths saturated with the solvent or by repeated fill and drain techniques.

3.3.1.2 Priming.- One brush coat of Chemlok 607 primer shall be applied to all cleaned aluminum surfaces that will be in contact with the sealing compound. The primer shall be air dried for not less than one half hour at 70-90°F.

3.3.2 Mixing.-

3.3.2.1 Filled Polymer.- Using a Hobart mixer or equivalent, glass fiber filler shall be mixed into the base polymer until a uniform blend is obtained. The filler shall consist of 25 - 30% by weight of the mixture.

NOTE: Prior to mixing, the glass fibers shall be dried for not less than 1 hour at 210-225°F. In addition, all containers and mixing equipment shall be thoroughly dry at the time of mixing.

3.3.2.2 Finished Sealant.- 24 parts by weight of the curing agent to each 100 parts by weight of the filled polymer shall be mixed. Mixing shall be done at room temperature.

NOTE: Each component may be heated up to 150°F to reduce their viscosities to facilitate mixing.

3.3.3 Application of Mixed Sealant.- The sealant shall be applied with a trowel, a caulking gun, or other similar device.

3.3.4 Cure.- Curing shall be as shown in Table II.

TABLE II — CURE SCHEDULE

Temperature	Time - Approximate	
	Tack Free	Full Cure
Room (75-80°F)	28 Hours	72 Hours
120 ± 10°F	24 Hours	48 Hours

4. QUALITY ASSURANCE PROVISIONS

4.1 Test Specimens.- Test specimens shall be in accordance with the ASTM D1876 and the following:

(a) Material shall be .020 inch thick 7075-T6 aluminum alloy

(b) Prior to the application of the sealant (adhesive), the adherends shall be --

1. Vapor degreased

2. Etched for approximately 10 minutes in the following solution:

Water	-	30 parts by weight
Conc H_2SO_4	-	10 parts by weight
$Na_2Cr_2O_7$	-	1 part by weight

Temperature of the solution during the etching shall be 150 ± 10°F

3. Rinsed in distilled water and air dried

4. Primed with one coat of Chemlok 607 primer (See Table I)

(c) Sufficient sealant shall be applied to the adherends to provide a bondline thickness of approximately 1/16 inch

4.2 Test Methods.- Sampling and frequency of testing for all requirements listed herein, except workmanship, shall be established by the cognizant quality control activity.

4.2.1 Examination of Product.- The entire filled area of all assemblies shall be visually examined for compliance with appearance and dimensional requirements.

4.2.2 Peel Strength.- Specimens described in 4.1 shall be tested at room temperature and at liquid nitrogen temperature in accordance with the method specified in ASTM D1876.

4.2.3 Thermal Shock.- Specimens described in 4.1 shall be given a thermal shock test consisting of 5 cycles of the following steps:

(a) Rapid immersion of the specimen in liquid nitrogen

(b) Removal of the specimen from liquid nitrogen and warming to room temperature

5. NOTES

5.1 This material is sensitive to moisture before it is cured. Therefore, care must be taken to keep all containers and mixing equipment clean and dry. Containers should be kept tightly closed when not in use to prevent degradation from atmospheric moisture.

5.2 The material used herein is sensitive to liquid oxygen. Under certain conditions, contact with liquid oxygen could result in an explosion.

"B"

HP 5-14

SEALING, GLASS FIBER FILLED POLYURETHANE COMPOUND, FOR LOX TANK APPLICATION

(REVISION A)

ELECTRONIC MFG. DIV.	HUGHES AIRCRAFT COMPANY CULVER CITY, CALIFORNIA	HP 5-14	REV. LTR. A
MISSILE MFG. DIV.	HUGHES PROCESS	PAGE 1 OF 4	
MTLS. TECHNOLOGY DEPT. L. Wiener / G. Peterson	SEALING, GLASS FIBER FILLED POLYURETHANE COMPOUND, FOR LOX TANK APPLICATION	ISSUE DATE 13 Feb 1963	REVISION DATE
		PREPARED BY G. Peterson	

1. SCOPE

Ⓐ 1.1 Scope.- This specification covers the sealing and filling of areas between liquid oxygen tank domes and outer walls of launch vehicles. Sealing material used is a refractory fiber filled polyurethane foam sealant.

NOTE: THIS MATERIAL SHALL NOT BE USED WHERE IT WILL BE DIRECTLY EXPOSED TO LIQUID OXYGEN (SEE 5.2).

2. APPLICABLE DOCUMENTS

2.1 The following document forms a part of this specification to the extent specified herein:

SPECIFICATIONS

Hughes Aircraft Company

HMS 16-1351 Plastic Resin, Polyurethane Elastomer, For Cold Temperature Sealant

3. REQUIREMENTS

3.1 Finished Product.-

Ⓐ 3.1.1 Workmanship.- The sealant shall be a fully cured cream colored elastomeric foam sealant. Unless otherwise specified by the engineering drawing, crevices shall be uniformly filled to a depth of approximately 4 inches. Inspection shall be as specified in 4.2.1.

Ⓐ 3.1.2 Density.- The fully cured sealant, shall have a density of 20 ± 2 lbs/cu ft. Testing shall be as specified in 4.2.2.

Ⓐ 3.1.3 Peel Strength.- Cured sealant shall have the following peel strength when tested as specified in 4.2.3:

Temperature	Peel strength, pounds per inch, min
Room	5.0
-320°F	1.0

Ⓐ 3.1.4 Thermal Shock.- Cured sealant shall show no visible signs of delamination when subjected to the thermal shock test specified in 4.2.4.

Ⓐ 3.2 Materials.- The materials required by this process shall be in accordance with Table I.

TABLE I -- MATERIALS

Component	Description	Mixture Parts by Weight, gms.	Applicable Specification
A	Adiprene L-100 (Resin) #3700 Fiberfrax Fibers[1]	100.0 42.6	HMS 16-1351 -
B	Castor Oil, USP XF 1034 Surfactant[2] Stannous Octoate (T-9)[3] Water (distilled)	24.8 2.0 1.1 0.4	- - - -
Primer	Chemlok 607[4]	-	-

1/ Carborundum Co., Niagara Falls, N. Y.
2/ General Electric Silicones, Corp., Waterford, N. Y.
3/ Metal & Thermit Corp., Rahway, N. J.
4/ Hugheson Chemical Co., Dist. R. D. Abbott Co., Los Angeles 32, Calif.

3.3 Procedure.-

3.3.1 Surface Treatments.-

3.3.1.1 Cleaning.- Aluminum tank walls shall be thoroughly cleaned with acetone or methyl ethyl ketone. Cleaning shall be accomplished by wiping the aluminum with clean cloths saturated with the solvent or by repeated fill and drain techniques.

3.3.1.2 Priming.- One brush coat of Chemlok 607 primer shall be applied to all cleaned aluminum surfaces that will be in contact with the sealing compound. The primer shall be air dried for not less than one half hour at 70 - 90°F.

Ⓐ 3.3.2 Mixing.-

3.3.2.1 Component A.- Using a Hobart mixer or equivalent, Fiberfrax fibers shall be mixed into the base polymer until a uniform blend is obtained. Containers shall be glass or metal (See 5.1).

NOTE: Prior to mixing, the Fiberfrax fiber shall be dried for not less than 1 hour at 210 - 225°F. In addition, all containers and mixing equipment shall be clean and dry at the time of mixing.

3.3.2.2 Component B.- Shall be mixed by weight in order listed in Table I.

3.3.2.3 Finished Sealant.- Component A shall be added to Component B. Mixing shall be done at room temperature. Each component may be heated to 150°F individually to facilitate mixing; however, heated mixed components pot life will be shorten appreciably (See 5.3).

Ⓐ 3.3.3 Application of Mixed Sealant.- The sealant shall be applied with a trowel, a caulking gun (preferred), or other similar device.

Ⓐ 3.3.4 Cure.- Curing shall be as shown in Table II.

TABLE II -- CURE SCHEDULE

Temperature	Time - Approximate	
	Tack Free	Full Cure
Room (75-80°F)	12 Hours	18 Hours
120 ± 10°F	6 Hours	10 Hours

4. QUALITY ASSURANCE PROVISIONS

4.1 Test Specimens.- Test specimens shall be in accordance with the ASTM D 1876 and the following:

(a) Material shall be .020 inch thick 7075-T6 aluminum alloy

(b) Prior to the application of the sealant compound, the adherends shall be --

1. Vapor degreased

2. Etched for approximately 10 minutes in the following solution:

Water	--	30 parts by weight
Conc H_2SO_4	--	10 parts by weight
$Na_2Cr_2O_7$	--	1 part by weight

Temperature of the solution during the etching shall be 150 ± 10°F.

3. Rinsed in distilled water and air dried

4. Primed with one coat of Chemlok 607 primer (See Table I)

(c) Sufficient sealant shall be applied to the adherends to provide a bondline thickness of approximately 1/16 inch.

4.2 Test Methods.- Sampling and frequency of testing for all requirements listed herein, except workmanship, shall be established by the cognizant quality control activity.

4.2.1 Examination of Product.- The entire filled area of all assemblies shall be visually examined for compliance with appearance and dimensional requirements.

Ⓐ 4.2.2 Density.- Density shall be determined in accordance with the method specified in ASTM D 1622.

Ⓐ 4.2.3 Peel Strength.- Specimens prepared as indicated in 4.1 shall be tested at room temperature and at liquid nitrogen temperature in accordance with the method specified in ASTM D 1876.

Ⓐ 4.2.4 Thermal Shock.- Specimens prepared as indicated in 4.1 shall be given a thermal shock test consisting of 5 cycles of the following steps:

(a) Rapid immersion of the specimen in liquid nitrogen

(b) Removal of the specimen from liquid nitrogen and warming to room temperature

5. NOTES

5.1 Moisture.- This material is sensitive to moisture before it is cured. Therefore, care must be taken to keep all containers and mixing equipment clean and dry. Containers should be kept tightly closed when not in use to prevent degradation from atmospheric moisture.

5.2 Caution.- The material described herein is sensitive to liquid oxygen. Under certain conditions, contact with liquid oxygen could result in an explosion.

Ⓐ 5.3 Pot Life.- Mix only enough sealant compound that can be applied in a 25-30 minute period at 75 ± 5°F.

Ⓐ 5.4 Improper Mixing.- The failure to cure of any mixed sealant compound after 18 hours, at 75 ± 5°F, is indicative of improper or incomplete mixing.

"C"

HP 5-14

SEALING, GLASS FIBER FILLED POLYURETHANE COMPOUND, FOR LOX TANK APPLICATION

(REVISION B)

CODE IDENT. NO. 82577

EL SEGUNDO MFG.	HUGHES AIRCRAFT COMPANY CULVER CITY, CALIFORNIA	HP 5-14	REV. LTR. B
TUCSON MFG.	HUGHES PROCESS	PAGE 1 OF 4	
MATLS. TECHNOLOGY DEPT.	SEALING, FIBERFRAX FILLED POLYURETHANE COMPOUND, FOR LOX TANK APPLICATION	ISSUE DATE 13 Feb 1963	REVISION DATE 12 Aug 63
		PREPARED BY H. Harvey	

1. SCOPE

1.1 Scope.- This specification covers the sealing and filling of areas between liquid oxygen tank domes and outer walls of launch vehicles. Sealing material used is a refractory fiber filled polyurethane foam sealant.

NOTE: THIS MATERIAL SHALL NOT BE USED WHERE IT WILL BE DIRECTLY EXPOSED TO LIQUID OXYGEN (SEE 5.2).

2. APPLICABLE DOCUMENTS

2.1 The following document forms a part of this specification to the extent specified herein:

SPECIFICATIONS

Hughes Aircraft Company

HMS 16-1351 Plastic Resin, Polyurethane Elastomer, For Cold Temperature Sealant

3. REQUIREMENTS

3.1 Finished Product.-

3.1.1 Workmanship.- The sealant shall be fully cured cream colored elastomeric foam sealant. Unless otherwise specified by the engineering drawing, crevices shall be uniformly filled to a depth of approximately 4 inches. Inspection shall be as specified in 4.2.1.

3.1.2 Density.- The fully cured sealant, shall have a density of 20 ±2 lbs/cu ft. Testing shall be as specified in 4.2.2.

3.1.3 Peel Strength.- Cured sealant shall have the following peel strength when tested as specified in 4.2.3:

Temperature	Peel strength, pounds per inch, min
Room	5.0
-320° F	1.0

3.1.4 Thermal Shock.- Cured sealant shall show no visible signs of delamination when subjected to the thermal shock test specified in 4.2.4.

(B) 3.2 Materials.- The materials required by this process shall be in accordance with Table I.

TABLE I -- MATERIALS

Component	Description	Mixture Parts by Weight, gms.	Applicable Specification
A	Adiprene L-100 (Resin) Fiberfrax Washed Fibers[1]	100.0 42.6	HMS 16-1351 -
B	Castor Oil, USP SF 1066 Surfactant[2] Benzyldimethylamine[3] Water (distilled)	24.8 2.0 1.46 (64 drops) 0.6 (16 drops)	- - - -
Primer	Chemlok 607[4]	-	-

1/ Carborundum Co., Niagara Falls, N. Y.
2/ General Electric Silicones, Corp., Waterford, N. Y.
3/ Miles Chemical Co., Elkhart, Indiana
4/ Hughson Chemical Co., Erie, Pa., Dist. R. D. Abbott Co., Los Angeles 32, Calif

3.3 Procedure

3.3.1 Surface Treatments.-

3.3.1.1 Cleaning.- Aluminum tank walls shall be thoroughly cleaned with acetone or methyl ethyl ketone. Cleaning shall be accomplished by wiping the aluminum with clean cloths saturated with the solvent or by repeated fill and drain techniques.

3.3.1.2 Priming.- One brush coat of Chemlok 607 primer shall be applied to all cleaned aluminum surfaces that will be in contact with the sealing compound. The primer shall be air dried for not less than one half hour at 70 - 90° F.

(B) 3.3.2 Mixing.-

3.3.2.1 Component A.- Using a Hobart mixer or equivalent, Fiberfrax fibers shall be mixed into the base polymer until a uniform blend os obtained. Containers shall be glass or metal (see 5.1).

NOTE: Prior to mixing, the Fiberfrax fiber shall be dried for not less than 1 hour at 210 - 225° F., then cool to room temperature prior to mixing. In addition, all containers and mixing equipment shall be clean and dry at the time of mixing.

3.3.2.2 Component B.- Shall be mixed by weight in order listed in Table I.

Ⓑ 3.3.2.3 Finished Sealant.- Component A shall be added to Component B. Mixing shall be done at room temperature.

3.3.3 Application of Mixed Sealant.- The sealant shall be applied with a trowel, a caulking gun (preferred), or other similar device.

Ⓑ 3.3.4 Cure.- Curing shall be as shown in Table II.

TABLE II -- CURE SCHEDULE

Temperature	Time - Approximate	
	Surface Tack Free	Full Cure*
Room (75-80° F)	8 Hours	18 Hours

*Physical properties will be substantially improved by post curing for 4 hours at 150° F.

4. QUALITY ASSURANCE PROVISIONS

4.1 Test Specimens.- Test specimens shall be in accordance with the ASTM D 1876 and the following:

(a) Material shall be .020 inch thick 7075-T6 aluminum alloy

(b) Prior to the application of the sealant compound, the adherends shall be --

1. Vapor degreased

2. Etched for approximately 10 minutes in the following solution:

Water	--	30 parts by weight
Conc H_2SO_4	--	10 parts by weight
$Na_2Cr_2O_7$	--	1 part by weight

Temperature of the solution during the etching shall be 150 ±10° F.

3. Rinsed in distilled water and air dried

4. Primed with one coat of Chemlok 607 primer (See Table I)

(c) Sufficient sealant shall be applied to the adherends to provide a bondline thickness of approximately 1/16 inch.

4.2 Test Methods.- Sampling and frequency of testing for all requirements listed herein, except workmanship, shall be established by the cognizant quality control activity.

4.2.1 Examination of Product.- The entire filled area of all assemblies shall be visually examined for compliance with appearance and dimensional requirements.

4.2.2 Density.- Density shall be determined in accordance with the method specified in ASTM D 1622.

4.2.3 Peel Strength.- Specimens prepared as indicated in 4.1 shall be tested at room temperature and at liquid nitrogen temperature in accordance with the method specified in ASTM D 1876.

4.2.4 Thermal Shock.- Specimens prepared as indicated in 4.1 shall be given a thermal shock test consisting of 5 cycles of the following steps:

(a) Rapid immersion of the specimen in liquid nitrogen

(b) Removal of the specimen from liquid nitrogen and warming to room temperature

5. NOTES

5.1 Moisture.- This material is sensitive to moisture before it is cured. Therefore, care must be taken to keep all containers and mixing equipment clean and dry. Containers should be kept tightly closed when not in use to prevent degradation from atmospheric moisture.

5.2 Caution.- The material described herein is sensitive to liquid oxygen. Under certain conditions, contact with liquid oxygen could result in an explosion.

5.3 Pot Life.- Mix only enough sealant compound that can be applied in a 25-30 minute period at 75 ±5° F.

5.4 Improper Mixing.- The failure to cure of any mixed sealant compound after 18 hours, at 75 ±5° F, is indicative of improper or incomplete mixing.

"D"

HMS 16-1351

PLASTIC RESIN, POLYURETHANE ELASTOMER, FOR COLD TEMPERATURE SEALANTS

CODE IDENT. NO. 82577

PREPARED BY	HUGHES AIRCRAFT COMPANY	16-1351
APPROVED	CULVER CITY, CALIFORNIA	
APPROVED	MATERIAL SPECIFICATION	PAGE 1 OF 3
APPROVED	PLASTIC RESIN, POLYURETHANE ELASTOMER, FOR COLD TEMPERATURE SEALANT	ISSUE DATE NOV 12 1962
APPROVED		REVISION DATE / REV.

1. SCOPE

1.1 Scope.- This specification covers a polyurethane resin which is to be used as a base polymer for a two part, cold temperature, plastic sealing compound.

2. APPLICABLE DOCUMENTS

2.1 There are no applicable governmental documents.

3. REQUIREMENTS

3.1 Qualification.- Material furnished under this specification shall be a product which has been tested and has passed the qualification tests specified herein. Qualified products are listed in Section 7 of this specification.

3.2 Material.- The resin shall be a clear, honeycolored, liquid polyurethane elastomer having the following properties:

3.3 Appearance.- The material shall be uniform in appearance, free of foreign material, and shall contain no lumps.

3.4 Viscosity.- The resin shall have a viscosity of from 14,000 to 19,000 cps. when tested as specified in 4.2.1.

3.5 Isocyanate Content.- The resin shall be a fully saturated polymer, which contains 4.0 to 4.3% isocyanate groups by weight, as determined in 4.2.2.

4. QUALITY ASSURANCE PROVISIONS

4.1 Classification of Tests.- The inspection and testing of material covered herein shall be classified as follows:

(a) Qualification Tests: Qualification tests are tests performed on samples submitted for approval as qualified products.

(b) Acceptance Tests: Acceptance tests are tests performed on individual lots that have been submitted for acceptance against a purchase order.

4.2 Qualification Tests.- The qualification tests shall consist of all the tests contained in this specification.

4.3 Acceptance Tests.- Acceptance tests shall consist of those tests contained herein that are deemed necessary to assure that the material meets the requirements of this specification.

4.4 Test Methods.-

4.4.1 Viscosity.- The viscosity of the base resin shall be measured with a Brookfield Viscosimeter, Model RVH, or equivalent. The base resin and viscosimeter shall be at a uniform temperature of 83-88°F during the test. The resin shall be thoroughly stirred with a spatula immediately before testing. Readings shall be taken when the pointer first assumes a steady position after the release of the clutch.

4.4.2 Isocyanate Content.- The test for determining the isocyanate content shall be conducted as follows:

To a 500 ml. Erlenmeyer flask, rinsed successively with water, alcohol, and benzene; dried at 100°C and cooled; add 40 ml. dry toluene. To this, add 50.00 ml. of a solution composed of 258.5 g. dry dibutylamine made up to 1000 ml. with dry toluene. Mix in the flask carefully. Weigh by difference on an analytical balance between 6.500 and 7.000 g. of the unfilled resin and transfer it to the flask. Carefully swirl the flask while slowly adding the resin. Wash down the sides of the flask with 10 ml. of dry toluene. Stopper the flask loosely and allow it to stand at room temperature for 15 minutes. Add 225 ml. of isopropyl alcohol from a 250 ml. graduated cylinder and and 0.8 ml. of bromcresol green indicator solution. Titrate with standardized 1N HCL solution while swirling the flask contents to effect rapid mixing. Consider the end point reached with the disappearance of the blue color and the appearance of a yellow color which persists for at least 15 seconds. Run a blank determination at the same time in exactly the same manner as above but omitting the resin.

Calculations:

$$\text{Assay} = \frac{(B-S) \times N \times E}{W \times 1000} \times 100$$

Where:

B = Ml. of HCl required to titrate blank

S = Ml. of HCl required to titrate resin

N = Normality of HCl

E = Equivalent weight of the resin in grams

W = Weight of resin in grams

4.4.3 Workmanship.- The material shall be visually examined to assure compliance with requirements not covered by other test methods.

5. PREPARATION FOR DELIVERY

5.1 Packaging.- Packaging shall be done in a manner that assures that the resin is not damaged or contaminated during shipment and storage.

5.2 Marking.- Containers of resin shall be legibly and permanently marked with the following information:

(a) This specification number

(b) Manufacturers Product Identification

(c) Date of Manufacturer

(d) Manufacturers Name and Address

6. NOTES

6.1 Intended Use.- Material described herein is intended for use in compounding a sealant material that can be used at temperature of -300°F.

7. QUALIFIED PRODUCTS

7.1 Procurement under this specification is limited to the products listed below:

Manufacturer's Designation	Manufacturer's Name and Address
Adiprene L-100	E. I. DuPont De Nemours and Co. Elastomers Division., Wilmington, Delaware

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